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**DEVELOPMENT OF A MOLTEN CARBONATE PROCESS
FOR REMOVAL OF SULFUR DIOXIDE
FROM POWER PLANT STACK GASES**

**PROGRESS REPORT NUMBER 2
PART II. PROCESS CHEMISTRY – REGENERATION
April 1, 1968 to October 27, 1968**

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**Atomics International
North American Rockwell**

P.O. Box 309
Canoga Park, California 91304

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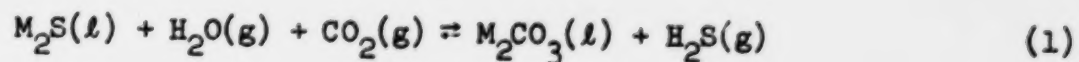
SUMMARY

The regeneration of sulfide-bearing melts with carbon dioxide and water vapor was studied. The regeneration reaction, $M_2S(l) + CO_2(g) + H_2O(g) = M_2CO_3(l) + H_2S(g)$ could be carried to completion at 500°C in a batch process within practical time limits (20 to 30 min.). The time required to complete the reaction was found to be limited by the input gas flow rate to melt volume ratio and the effective equilibrium constant for the regeneration reaction. Foreign metal impurities (Fe, V, Mo, Sn, Ge) in the melt reduced the sulfide activity in varying amounts causing a reduction in the hydrogen sulfide content in the off-gas stream. Calcium impurity did not affect the regeneration process. The effect of iron, a potential reduction catalyst, was studied in detail. Iron caused melts to foam during regeneration under certain conditions, and was also found to precipitate along with some sulfide during the regeneration process. The iron-sulfide precipitate could be completely recovered from the regenerated melt by filtration and reused as a reduction catalyst. The optimum rates and utilization of regeneration gases will require low temperatures (< 500°C) and carbon dioxide equilibrium pressure less than 0.5 atmospheres. The decrease in the effective equilibrium constant for the regeneration process with increase in carbon dioxide pressure was postulated to be due to the interaction of carbon dioxide with sulfide to form a series of thiocarbonates. Cycle tests showed that the sulfur can be removed completely and revealed no problems due to cycling on the quality of the carbonate melt.

I. INTRODUCTION

A. BACKGROUND

The regeneration of sulfide-bearing carbonate melts and the recovery of sulfur from these melts is the third step in the Molten Carbonate Process. It follows the absorption step, where carbonate is converted to sulfite, and the reduction step, where the sulfite is reduced to sulfide. The regeneration converts the sulfide back to carbonate plus hydrogen sulfide; it can be accomplished according to the reaction



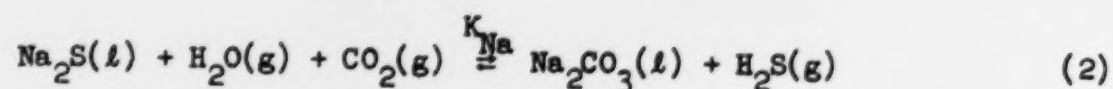
where M stands for the mixture of lithium, sodium and potassium cations in the proportions found in a eutectic mixture of their carbonates.

Regeneration tests performed during the previous report period⁽¹⁾ showed that sulfide-bearing melts, formed by the reduction of sulfate-bearing melts, could be regenerated to carbonate for recycling to the scrubber, and that the sulfur could be recovered as hydrogen sulfide with good efficiency. In addition, the regeneration reaction was demonstrated to be reversible, and preliminary estimates were made for the value of the equilibrium coefficient as a function of temperature. During the present report period, regeneration studies continued, with the objective to optimize the regeneration process for testing in a pilot plant. The results of these studies are the subject of this report. Most of the earlier results, from the previous report period, are included for comparison and completeness.

B. THERMODYNAMICS OF THE REGENERATION PROCESS

It is not possible to perform a rigorous thermodynamic analysis of the reactions involved in regenerating a melt of mixed alkali metal carbonates containing sulfide because (1) thermodynamic data are not available for

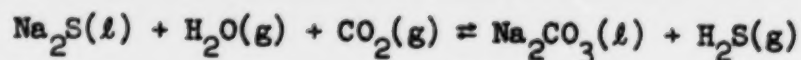
potassium and lithium sulfide, (2) the activities of sulfide and carbonate in a molten mixture are not known, (3) the species existing in these solutions are not known (thiocarbonates may be present), and (4) the extent of interaction of carbon dioxide, water and hydrogen sulfide with the melt is not known. However, there is sufficient data available on molten sodium carbonate and sodium sulfide that the regeneration of sodium carbonate can be studied theoretically, and compared with experimental data available in the literature. The reaction for the regeneration of sodium sulfide is



The standard free energy changes for reaction 2 and the equilibrium constants at several temperatures were calculated from available thermodynamic data.⁽²⁾ These values are listed in Table 1.

TABLE 1

Free Energy and Equilibrium Constants for the Reaction:

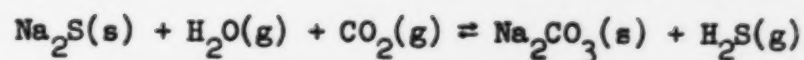


Temp.		ΔF° (Kcal/g mole)	K(atm ⁻¹)
(°C)	(°F)		
427	800.6	-5.95	71.94
527	980.6	-3.16	7.30
627	1160.6	-0.53	1.34
727	1340.6	+1.96	0.37
827	1520.6	+4.33	0.14
927	1700.6	+6.60	0.063

The corresponding values at two temperatures for the regeneration reaction involving solid sodium sulfide and carbonate are listed in Table 2.

TABLE 2

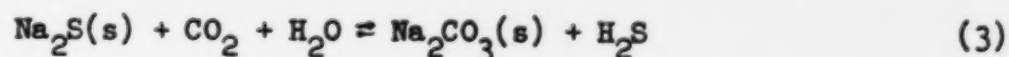
Free Energy and Equilibrium Constants for the Reaction:



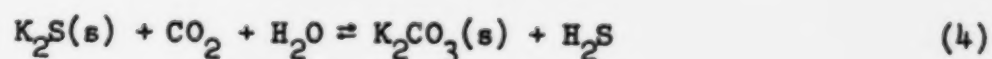
Temperature		ΔF° (Kcal/g mole)	K(atm ⁻¹)
(°C)	(°F)		
427	800.6	-8.18	352.0
527	980.6	-4.86	21.4
627	1160.6	-1.70	2.59
727	1340.6	+1.34	0.51
827	1520.6	+4.29	0.14

From Tables 1 and 2 it can be seen that the regeneration reaction is thermodynamically more favorable at the lower temperature and with solid salts.

Experimental studies of the equilibria for sodium and potassium salts:



and



have been carried out by Koszegi and Rosen.⁽³⁾ They found that the experimental values for the sodium salt system could be represented quite well with the equation

$$\log K = \frac{5700}{T} - 6.03 \quad (5)$$

when log K was plotted as a function of the reciprocal of the absolute temperature, T⁻¹. The data for the potassium sulfide system were represented by the equation

$$\log K = \frac{14000}{T} - 16.0 \quad (6)$$

Values for K calculated from equations (5) and (6) are compared graphically in Figure 1 with the values given in Tables 1 and 2. It can be seen from Figure 1 that the experimental line for the equilibrium constant, K, for the solid sodium sulfide-sodium carbonate system falls between the calculated lines for the solid and liquid systems. The agreement of the experimental data with the calculated curve for the solid sodium salts is, however, quite good.

From Figure 1, the reaction of solid potassium sulfide to form the solid carbonate appears more favorable than that of sodium sulfide at the lower temperatures (below 570°C) and less favorable above 570°C. At 500°C, the K value (150 atm^{-1}) for the potassium sulfide reaction is about 6 times larger than the value for the sodium sulfide reaction. Although the data for solid or molten lithium sulfide systems are not available, the equilibrium constant for the molten sulfide-carbonate system should be reasonably close to the values plotted in Figure 1. Otherwise, a significantly lower value for the molten eutectic system would require an assumption that the lithium ion could tie up two or more sulfide ions in the form of a stable charged ion, or that lithium could reduce the activity of sulfide by a substantial amount. There is no evidence from the literature that this can occur. Thus, the data shown in Figure 1 are probably representative of the eutectic system and serve as a useful guide in the study of the regeneration of sulfide-bearing carbonate melts.

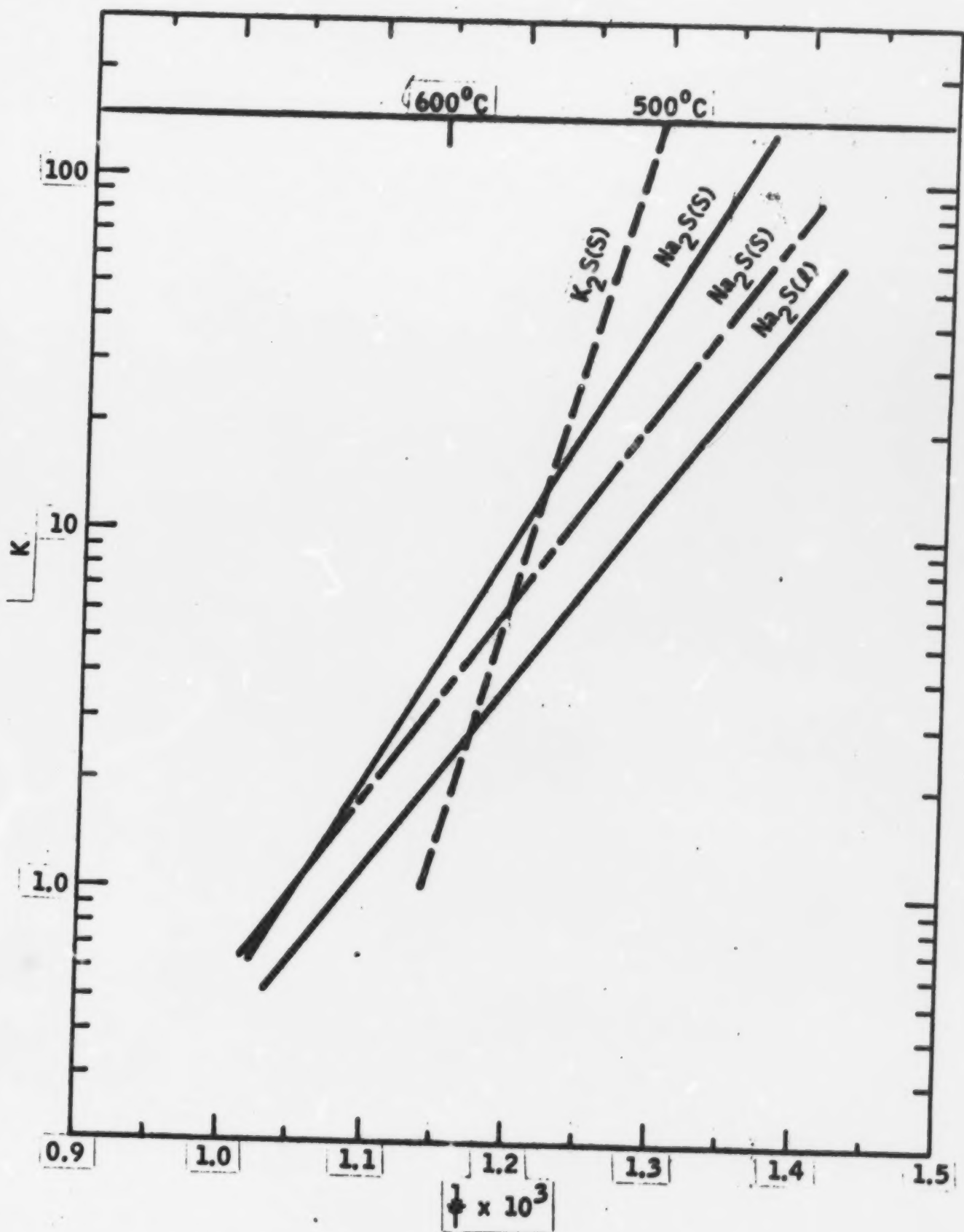


Figure 1. Regeneration Equilibrium Constants for Pure Salts

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II. EXPERIMENTAL

A. MATERIALS

Gases. The gases used in the regeneration studies, carbon dioxide, helium, hydrogen sulfide, and argon were all technical grade, from cylinders.

Salts. All of the carbonate and sulfate salts were analytical reagent grade chemicals. Reagent grade sodium sulfide hydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) was used after most of the water had been removed by heating to 120°C in vacuum for several days. Sodium sulfide dried in this manner was 95-99% pure. Technical grade iron (ferrous) sulfide, 4-20 mesh, and technical grade iron pyrites were used in obtaining solubility data on iron compounds in the eutectic carbonate.

B. APPARATUS

The regeneration tests consisted of passing feed gases containing carbon dioxide and water vapor through carbonate melts containing sulfide. During these tests, the exit gases were passed through condensers to remove excess water. The dried gases were analyzed periodically by gas chromatography and then scrubbed to recover gaseous products.

Most of the regeneration tests were carried out at a system pressure of 1 atm. Figure 2 shows a sketch of the apparatus (discussed below in more detail) used for these tests. The system was also modified for regeneration tests at higher pressures. The modified apparatus is shown in Figure 3.

The flow rates of the different gas streams were measured with rotameters (Matheson Flowmeter tubes) which had been calibrated against a soap-film meter. During measurements, the flowmeter floats oscillated somewhat and slight drifts occurred. The errors of the measured gas volumes of helium and carbon dioxide may amount to a few percent.

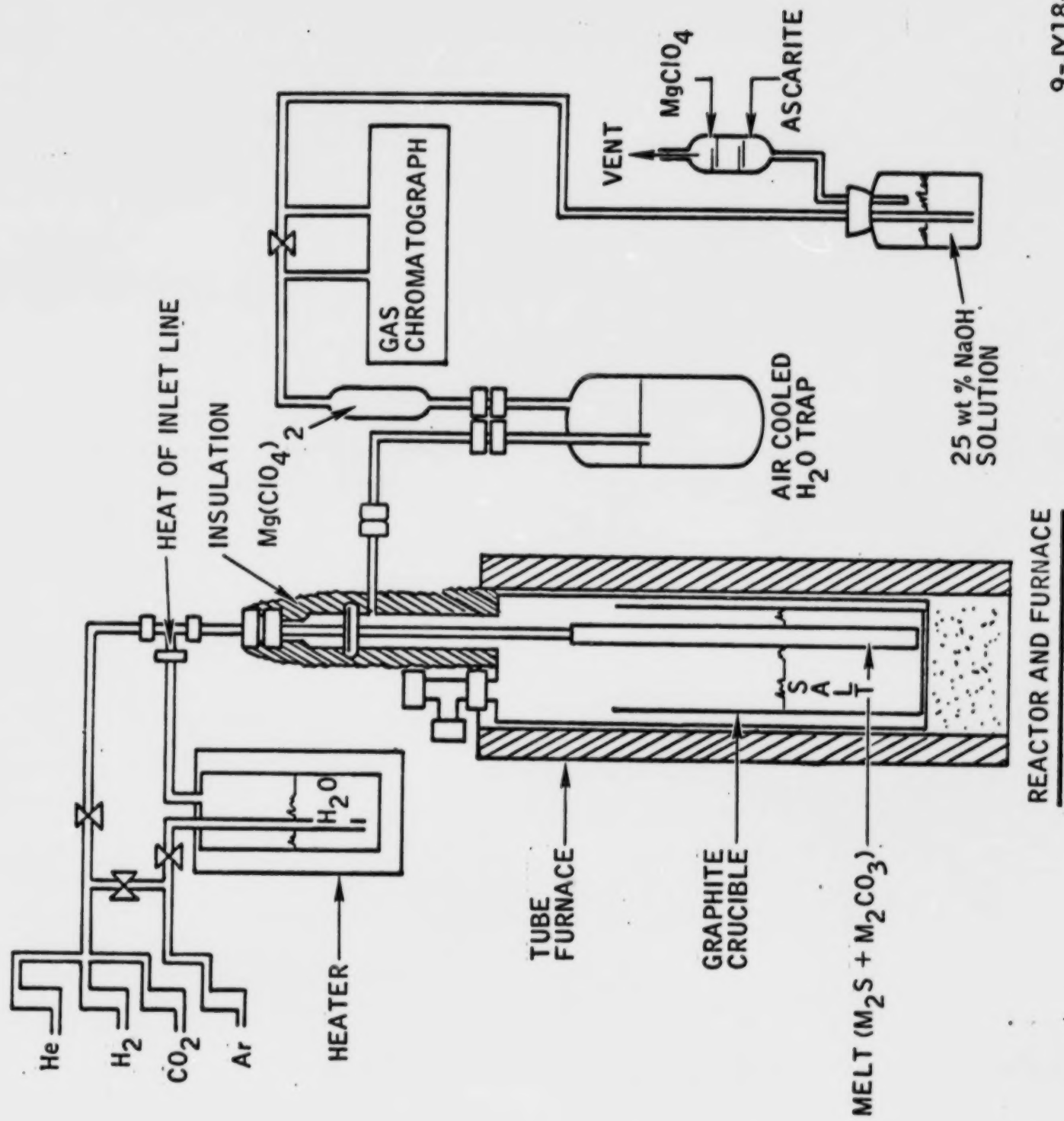


Figure 2. Regeneration Test System

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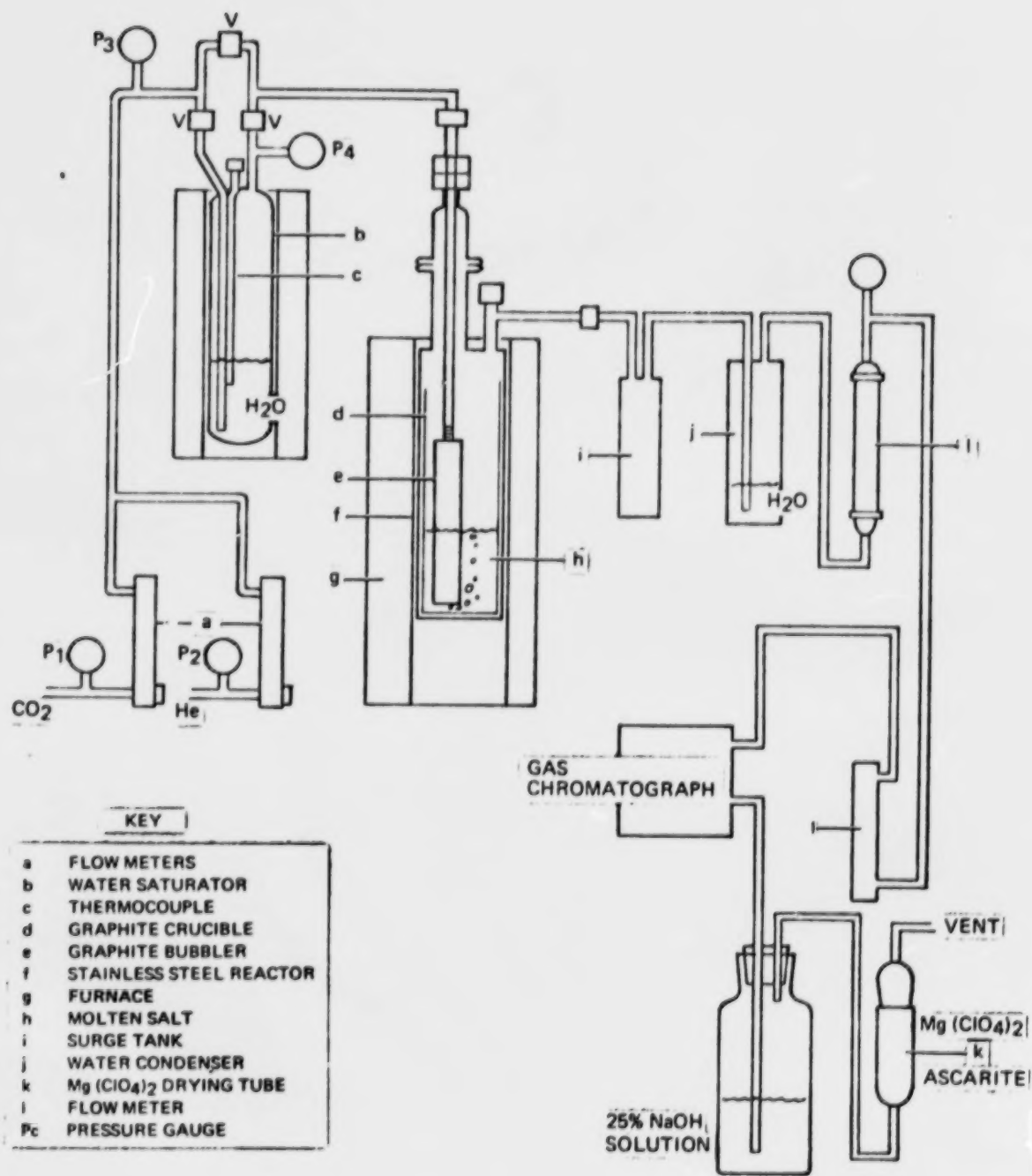


Figure 3. High Pressure Regeneration Test System

Water Saturator. The water saturator consisted of a stainless steel vessel (4 in. OD x 11 in. long) partially filled with distilled water and fitted with stainless steel inlet and exit tubes. The vessel was wrapped with electrical heating wire and covered with insulation; it was also fitted with a Weston thermometer with 1° divisions. The temperature was controlled with an ON-OFF Fenwol regulator. The temperature changed to some extent (up to 10°C) during a test, with the greatest change occurring when high feed gas flow rates were used. However, the temperature was recorded at frequent intervals so that the water temperature at any given time could usually be determined to within 2°C. Spot checks of the amount of water collected from the effluent over a set interval were made. The amount of water collected indicated that the partial pressure of the water-saturated feed gases was about 85-95% of the equilibrium pressure indicated by the water saturator temperature.

Reactor. The main body of the reactor, shown in Figure 4, was constructed of type 304 stainless steel cylinder 12 in. long by 3 in. OD. Top and bottom plates were welded to this cylinder. The top plate was fitted with a 3/8 in. OD steel tube for sampling and a 1-1/4 in. OD tube for insertion of the bubbler.

Absorbers. The effluent regeneration gases were passed through 20 wt% sodium hydroxide solutions to collect hydrogen sulfide and most of the carbon dioxide, and then through ascarite traps to remove the remaining carbon dioxide. Each sodium hydroxide absorber consisted of about 500 ml of 20 wt% sodium hydroxide solution contained in a 1-liter polypropylene bottle. A gas inlet tube of 1/4 in. Tygon reached near the bottom of each absorber. At high feed gas flow rates (above 0.8 l/min), two absorbing solutions were used in series.

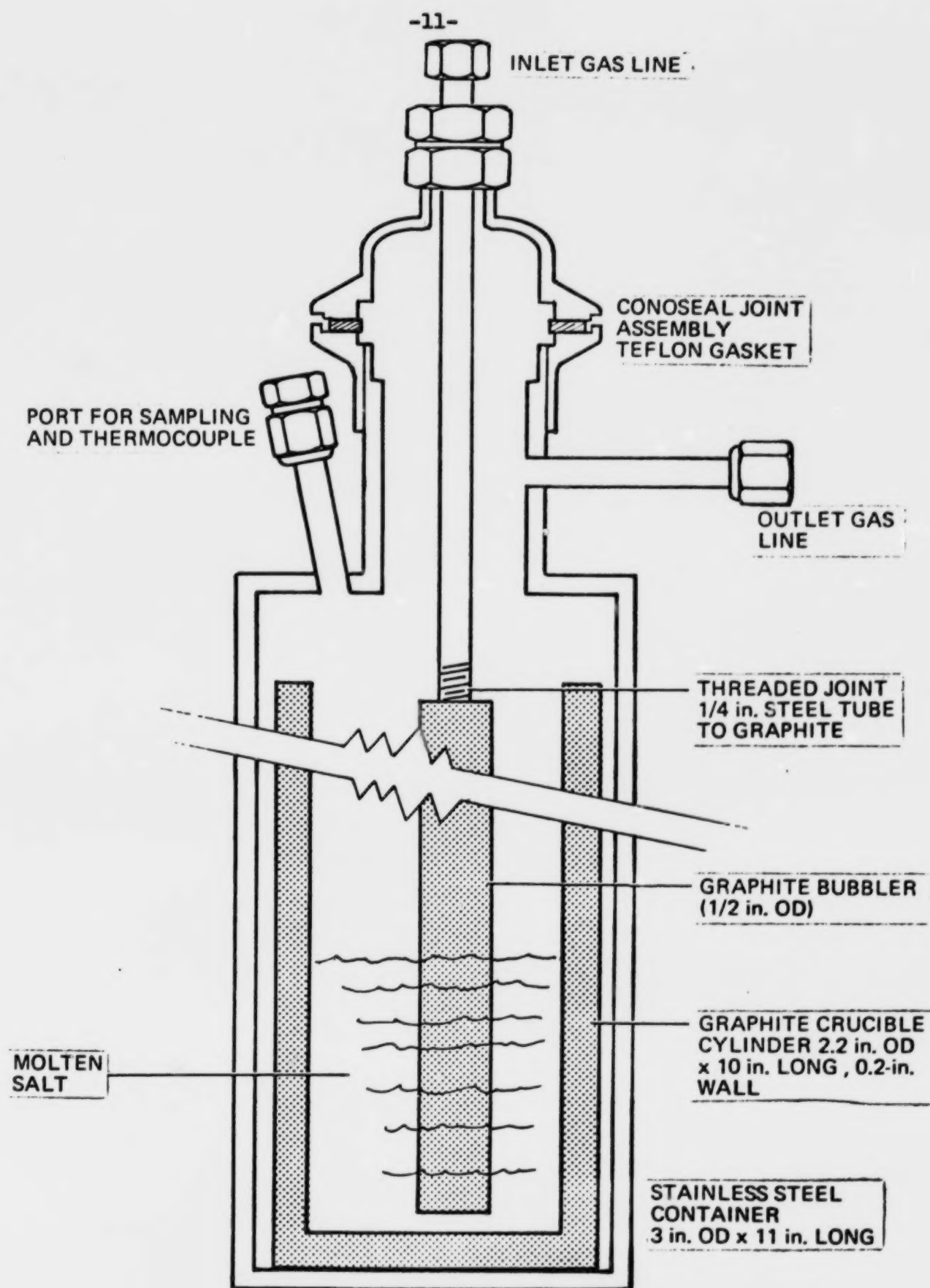


Figure 4. Regeneration Reactor

Pressure Measurements. Pressure measurements during regeneration tests where the system pressure was greater than 1 atm were made with standard bourdon-tube type pressure gauges.

C. ANALYSIS

The analytical procedures used for analysis of solidified melt samples for sulfide, sulfite, carbonate, sulfate, and total sulfur have been described previously.⁽¹⁾ The iron contents of melt samples were found by a colorimetric method using 1,10-phenanthroline.

D. TEST PROCEDURE

1. Bubble-Through Regeneration Tests

Most of the regeneration tests were tests in which gases were bubbled through melts. The regeneration gases, carbon dioxide and steam (sometimes diluted with a helium carrier gas) were bubbled through from 50 to 200 g of carbonate melts in the apparatus shown in Figure 2. The procedure was essentially the same in each test.

Melt Preparation and Sampling. The sulfide-bearing melts were prepared in three different ways: (1) reducing sulfate-bearing melts with hydrogen or carbon monoxide, (2) mixing together suitable amounts of carbonate and sodium sulfide, and (3) by acid-base reactions in molten carbonates. The reduced melts were obtained from reduction studies of sulfate-bearing melts and their preparation is discussed in a separate report.⁽⁴⁾ The melts made by acid-base reactions were prepared by treating carbonate melts with hydrogen sulfide or by reacting sodium hydroxide and hydrogen sulfide in molten carbonate.

After the melts were prepared, they were heated or cooled to the desired test temperature. During this period, an inert gas (argon or helium) was passed through the melt. During various stages of the tests, melt samples

were taken by withdrawing 3 to 5 g samples into a 4 mm Pyrex tube. These samples were used for melt analysis.

It was necessary to know the melt volume during the tests so that material balances could be made more accurately. The melt volume changes were also useful as an indication of changes occurring in the reactor, e.g., foaming or melt leakage through broken crucibles. The melt volume was determined by measuring the melt height as indicated by the melt line on the outside surface of the Pyrex sampling tube inserted to the bottom of the crucible.

Start of Regeneration Test. Shortly after the reaction temperature was reached and the melt samples were taken, the inert gas flow was diverted through the water saturator. Then the carbon dioxide flow was started and the helium flow stopped. In some tests, dry carbon dioxide alone was passed through the melt until carbon dioxide was detected in the effluent gases. Then the carbon dioxide was diverted through the water saturator before passing through the melt.

Effluent Gas. Most of the water in the effluent gases was collected in an air-cooled condenser and the remainder in a magnesium perchlorate trap. The dry effluent gas then passed through the sampling chamber of a gas chromatograph where samples were analyzed periodically. The gases passed from the gas chromatograph chamber to absorbers.

End of Test. In most tests, the regeneration reaction was continued until the hydrogen sulfide content of the effluent had decreased to 1 vol% or less. Then the carbon dioxide flow was stopped and the helium flow was started, bypassing the water saturator. A final melt sample was taken and then the reactor was removed from the furnace and cooled while inert gas was

passed over the melt. After the reactor had cooled, it was cut open and the graphite crucible was removed and the contents inspected. In cases where a deposit had formed above the bulk of the melt, samples of the deposit were taken for analysis.

2. Cycle Tests

Cycle tests were performed in which several cycles involving an absorption, a reduction and a regeneration step were carried out in that order. These tests were carried out in the same apparatus used for the bubble-through regeneration tests.

Absorption Step. In the absorption steps for the first two tests, sulfur was added to the carbonate melt by absorption of sulfur dioxide. This was done in order to test for possible changes in absorption efficiency from cycle to cycle. In later cycle tests, sulfur was added to regenerated melts by adding sodium sulfate along with enough potassium and lithium carbonate to keep the cation ratios correct.

Reduction Step. After the absorption step, the melt was heated to the desired temperature (usually 600°C) and the sulfate was reduced to sulfide with hydrogen.

Regeneration Step. After the reduction step, the melt temperature was lowered to the desired temperature (usually 500°C) and the regeneration step was carried out as described above. Melt samples and melt volumes were taken before and after each step in each cycle.

III. EXPERIMENTAL RESULTS

A. BUBBLE-THROUGH REGENERATION TESTS OF REDUCED MELTS

1. Purpose

A number of sulfide-bearing carbonate melts, which were regenerated, were made by reducing sulfate-bearing melts. These tests were carried out to determine the effects of the reducing conditions on the regeneration process. The reducing conditions included variations in type of reducing agent, temperature, pressure, and type of catalyst or impurity.

2. Classification of Reduced Melts

The reduced sulfide-bearing carbonate melts were made by reducing sulfate-bearing melts with hydrogen or carbon monoxide. These reduced melts are placed in three classifications:

Class 1: Sulfate-carbonate melts containing only alkali metal cations reduced with either hydrogen or carbon monoxide.

Class 2: Sulfate-carbonate melts containing alkali metal cations and one additional cation (excluding iron) reduced with hydrogen.

Class 3: Sulfate-carbonate melts containing alkali metal cations and iron, reduced with hydrogen or carbon monoxide.

3. Organization of Data from Regeneration Tests on Reduced Melts

The experimental data from all of the regeneration tests are summarized in two Tables. The first Table (Table 3) summarizes the reduction and regeneration test conditions for each regeneration test. The second Table (Table 4) summarizes the melt conditions and the melt composition data for each regeneration test. Additional data are shown in a figure for each regeneration test. The figure shows the inlet and exit gas composition and other data plotted as a function of regeneration time.

Table 3. BUBBLE THROUGH REGENERATION TESTS OF REDUCED MELTS

Test No.	Reduction Conditions				Regeneration Conditions				Remarks		
	Temp (°C)	Catalyst		Reducing Agent	Pressure (atm)	Regenerating Gases					
		Composition	Conc. (wt %)			Kind	Pressure (atm)	CO ₂ (ml/min)		H ₂ O Sat. Temp (°C)	He (ml/min)
1	2	3	4	5	6	7	8	9	10	11	12
1	600	0	0	H ₂	1	1	300	84-91	100	500	Pure alkali metal salt melts
2	700	0	0	H ₂	1	1	100	57-95	100-200	500	Higher temperature during reduction
3	600	0	-	CO	1	1	800	77-97	0	500	Reduction with carbon monoxide
4	600	Sn	5.0 Sn	H ₂	1	1	150	83-91	180-200	500	Tin impurity
5	600	GeO ₂	3.2 Ge	H ₂	1	1	150	88-90	180	500	Germanium impurity
6	600	Mo	4.2 Mo	H ₂	1	1	150	89-92	180	500	Molybdenum impurity
7	600	VO ₂	2.2 V	H ₂	1	1	150	76-95	180	500	Vanadium impurity
8	600	FeSO ₄	2.4 Fe	H ₂	1	1	150	85-95	200	500	Iron impurity from reduction
9	600	Fe powder	2.4 Fe	H ₂	1	1	100-150	86-95	100	500	Different form of iron added in reduction
10	600	FeS	2.4 Fe	H ₂	1	1	75	87-94	100-200	500	Different form of iron added in reduction
11	650	FeSO ₄	2.4 Fe	H ₂	1	1	100-150	84-98	100-200	600	Higher reduction and regeneration temp with iron
12	700	FeSO ₄	2.4 Fe	H ₂	1	1	150	78-91	180	500	Higher reduction temp with iron
13	650	FeSO ₄	2.4 Fe	H ₂	3	1	150	75-93	180	500	Higher pressure reduction with Fe
14	650	FeSO ₄	2.4 Fe	H ₂ + H ₂ O	1	1	850-150	72-92	180	500	Reduction with H ₂ and H ₂ O with Fe
15	600	FeSO ₄	2.4 Fe	H ₂	2	1	150	88-89	180	425	Lower regeneration temperature
16	615	(Fe)	2.3 Fe	H ₂	1	1	150	87-90	180	498	Separate CO ₂ and H ₂ O treatment
17	600	FeSO ₄	2.4 Fe	H ₂	3	1	150	90	180	490	Filtration of melt at stages of regeneration
18	600	FeSO ₄	2.4 Fe	H ₂	1	3	130	90-125	350	500	Higher pressure during regeneration
19	700	FeSO ₄	2.4 Fe	CO	1	1	800	77-84	0	500	Iron catalyzed carbon monoxide reduction
20	650	FeSO ₄	2.4 Fe	H ₂	1	1	800	78-80	0	500	Calcium impurity
21	650	FeSO ₄	0.1 Fe	H ₂	1	1	800	79-86	0	500	Low melt iron content

TABLE 4

Summary of Data for Regeneration of Reduced Melts

Regen. Test #	Melt Conditions				Melt Composition (wt %)			
	Temp. (°C)	Treatment Completed	Time (min)	Melt Volume(ml)	M ₂ CO ₃	H ₂ S	H ₂ SO ₄	Other
1	600	Reduction		115	77.3	17.6	1.70	-
	500	cooled		-	-	-	-	-
	500	CO ₂	5	-	-	-	-	-
	500	CO ₂ + H ₂ O	148	103	97.6	0.0	1.67	-
2	700	Reduction		136	79.0	12.8	8.9	-
	500	cooled		101	88.2	13.9	-	-
	500	CO ₂	55	117	81.0	11.3	-	-
	500	CO ₂ + H ₂ O	170	117	92.7	0.11	-	-
3	600	Reduced		72	70.9	10.6	-	-
	500	CO ₂ , H ₂ O	45	72	84.7	0.9	-	-
4	600	Reduction		125	74.2	(11.6) ^a	-	-
	500	cooled		106	-	-	-	-
	500	CO ₂	60	117	89.6	(4.5)	-	-
	500	CO ₂ , H ₂ O	100	130	97.2	(2.6)	-	-
5	600	make-up-melted		120	69.4	7.9	14.5	Ge
	500	cooled		120	69.0	7.9	-	-
	500	CO ₂ , H ₂ O	195	120	80.7	0.55	13.8	-
	490	CO ₂ , H ₂ O	110	122	79.3	0.12	14.0	-
6	600	Make up-melted		125	74.2	0.2	25.1	4.2 Mo
	600	reduced		106	72.4	14.3	5.0	-
	500	cooled		-	76.3	11.9	-	-
	500	CO ₂ , H ₂ O	320	-	93.3	0.13	-	-
7	650	Make up-melted		125	69.5	0	26.2	2.3 V
	600	reduced		117	76.1	15.8	5.7	-
	500	cooled		117	74.9	15.9	-	-
	500	CO ₂ , H ₂ O	300	106	91.9	0.96	-	-

TABLE 4 (cont'd)

Summary of Data for Regeneration of Reduced Melts

Regen. Test #	Melt Conditions				Melt Composition (wt %)			
	Temp. (°C)	Treatment Completed	Time (min)	Melt Volume(ml)	M ₂ CO ₃	M ₂ S	M ₂ SO ₄	Other
8	600	Reduction		-	73.5	17.5	< 0.1	-
	500	cooled		-	83.0	17.2	-	-
	500	CO ₂	20	125	83.0	17.2	-	2.0 Fe
	500	CO ₂ + H ₂ O	144	81	101.2	0.16	-	0.01 Fe
9	600	Reduction		-	78.6	18.2	-	-
	500	cooled		101	78.0	16.4	-	-
	500	CO ₂	60	122	86.7	13.5	-	-
	500	CO ₂ + H ₂ O	150	100	94.8	0.29	-	-
10	600	Reduction		83	77.3	24.1	-	-
	500	cooled		78	79.5	20.9	-	-
	500	CO ₂	80	82	86.5	19.4	-	-
	500	CO ₂ + H ₂ O	150	46	101.1	0.28	-	-
11	650	Reduction		126	77.5	17.4	0.9	-
	600	cooled		107	86.2	19.5	-	2.1 Fe
	600	CO ₂		117	96.0	16.0	-	2.2 Fe
	600	CO ₂ , H ₂ O		100	102.9	4.2	-	0.93 Fe
	600	CO ₂ , H ₂ O		-	102.1	5.8	-	1.1 Fe
	475	He purge		81	104.5	3.6	-	1.6 Fe
12	700	Reduction		125	75.9	17.0	-	-
	500	cooled		117	75.8	20.6	-	-
	500	CO ₂ , H ₂ O	230	106	94.3	4.5	-	-
	500	He	126	100	89.6	8.5	-	-
13	650	Make up-melted		125	67.8	0	25.1	2.5 Fe
	650	reduced		100	78.5	19.8	0	-
	500	CO ₂ , H ₂ O	210	90	100.0	1.53	-	-

TABLE 4 (cont'd)

Summary of Data for Regeneration of Reduced Melts

Regen. Test #	Melt Conditions				Melt Composition (wt %)			
	Temp. (°C)	Treatment Completed	Time (min)	Melt Volume(ml)	M ₂ CO ₃	M ₂ S	M ₂ SO ₄	Other
14	650	Make up-melted		125	72.7	0.5	26.4	2.5 Fe
	650	reduced		-	71.9	18.9	0.7	-
	500	M ₂ SO ₄ added		160	78.5	13.6	-	-
	500	CO ₂ , H ₂ O	160	125	95.5	3.9	-	-
15	600	Make up-melted		135	61.5	11.2	24.0	-
	600	reduced		135	67.2	25.2	3.2	-
	420	cooled		135	81.7	19.4	-	-
	425	CO ₂ , H ₂ O	206	120	100.7	3.7	-	-
16	420	Regen. melt		-	100.7	3.7	-	-
	615	added 75g, M ₂ SO ₄ reduced		-	79.0	25.8	-	2.3 Fe
	500	CO ₂	209		82.2	18.7	-	1.6 Fe
	495	H ₂ O	166	-	78.5	15.8	-	1.6 Fe
	495	CO ₂	184	-	84.3	13.1	-	-
	495	CO ₂ , H ₂ O	255	-	101.8	0.7	-	-
18	600	reduced		106	75.7	14.3	1.54	2.4 Fe
	500	CO ₂ , H ₂ O	220	102	100.3	6.8	-	-
19	700	reduced		80	72.1	16.8	1.23	-
	500	CO ₂ , H ₂ O	67	80	82.9	4.5	1.9	-
20	650	reduced		122	63.2	14.3	-	-
	500	CO ₂ , H ₂ O	80	94	85.9	3.0	8.1	-
21	600	reduced		72	81.3	12.1	5.6	-
	500	CO ₂ , H ₂ O	80	72	92.5	0	-	-

Data for Test 17 given in separate table (Table 5)

TABLE 4 (cont'd)

Summary of Data for Regeneration of Reduced Melts

Regen. Test #	Melt Conditions				Melt Composition (wt %)		
	Temp. (°C)	Treatment Completed	Time (min)	Melt Volume(ml)	M ₂ CO ₃	M ₂ S	M ₂ SO ₄
30	500	make up	—	108	91.84	4.70	4.29
	500	CO ₂ , H ₂ O	20	108	95.56	0.52	4.55
	500	CO ₂ , H ₂ O	44	93	94.75	0.07	—
31	500	make up	—	114	92.0	9.31	3.62
	500	CO ₂ , H ₂ O	20	114	103.0	0.69	4.17
	500	CO ₂ , H ₂ O	31	114	101.8	0.24	—

Table 3, which summarizes the reduction and regeneration test conditions, includes the following data: Column 1 of Table 3 gives the regeneration test number, Columns 2-6 give the reduction conditions (melt temperature during reduction, concentration of the major non-alkali metal impurity, kind of reducing agent used, and system pressure during reduction). Columns 7-11 give the conditions used to regenerate the melt. These include the system pressure, the carbon dioxide feed rate in ml/min., the water saturator temperature, the melt temperature, the feed rate of the helium carrier gas, and the melt temperature during regeneration. Column 12 gives the major variation for a given test.

Table 4 summarizes the melt composition data obtained from melt samples. Before and after each melt was regenerated, melt samples were taken for analysis and the volume of melt in the reactor was determined. Table 4 contains the following data: Column 1 gives the regeneration test number, and columns 2-5 give the melt conditions, including the melt temperature, description and duration of treatment completed, and the melt volume prior to withdrawing the melt sample. (The duration of treatment in Column 4 includes only the time of the regeneration test). Columns 6-9 give the composition of the melt samples. The composition data includes the melt carbonate, sulfide and sulfate weight percentages and also the major impurity content of the melt.

During the regeneration of the melts described in Tables 3 and 4, the composition (hydrogen sulfide and carbon dioxide contents) of the exit gas was determined at frequent intervals until the hydrogen sulfide content of the exit gas had decreased to less than one percent. Figures 5 to 25 show the dry exit gas composition plotted against regeneration time for tests 1-21. Since the inlet gas feed rates and water saturator temperatures were varied to some

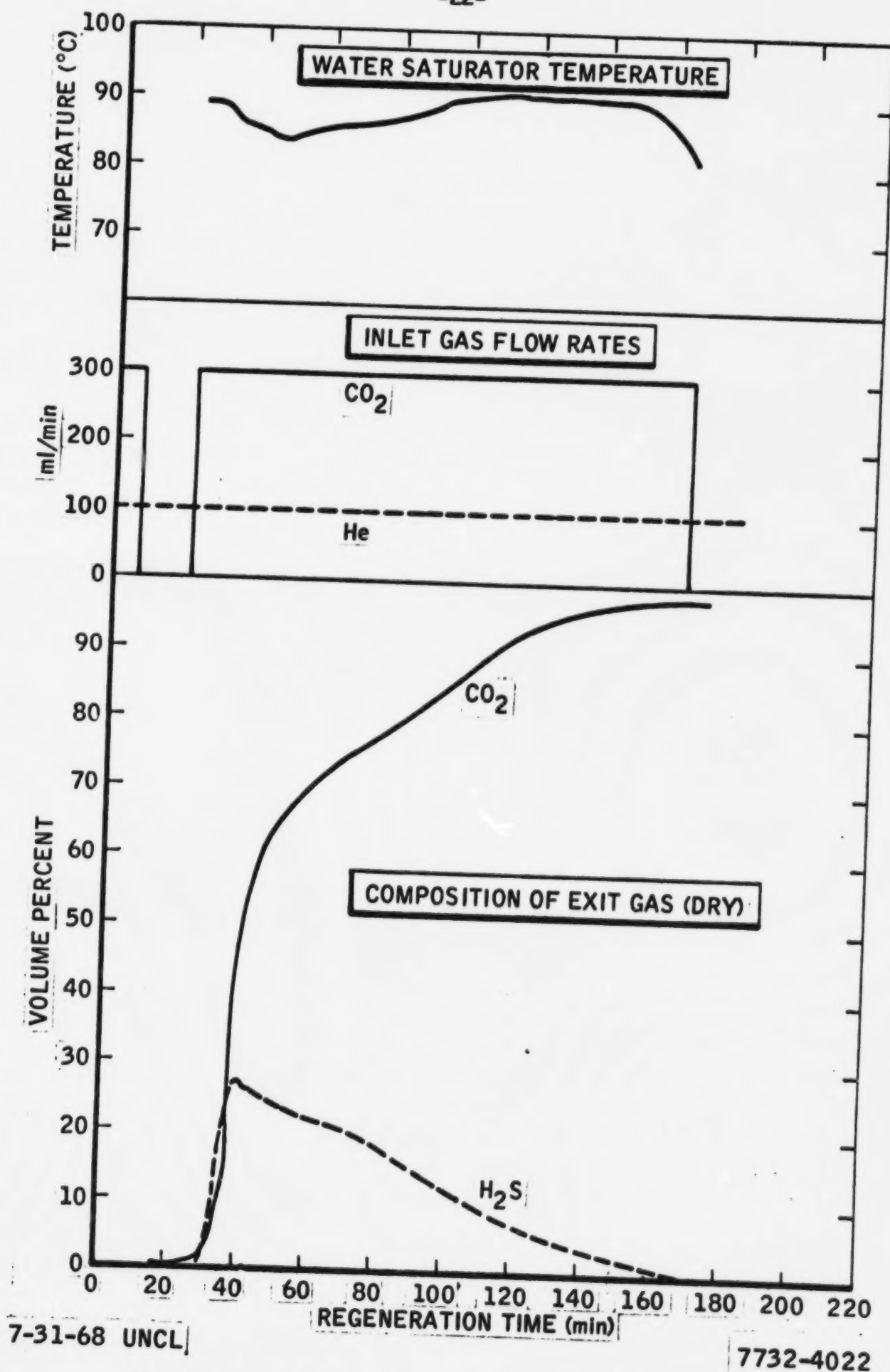


Figure 5. Regeneration of a Pure Melt (Test 1)

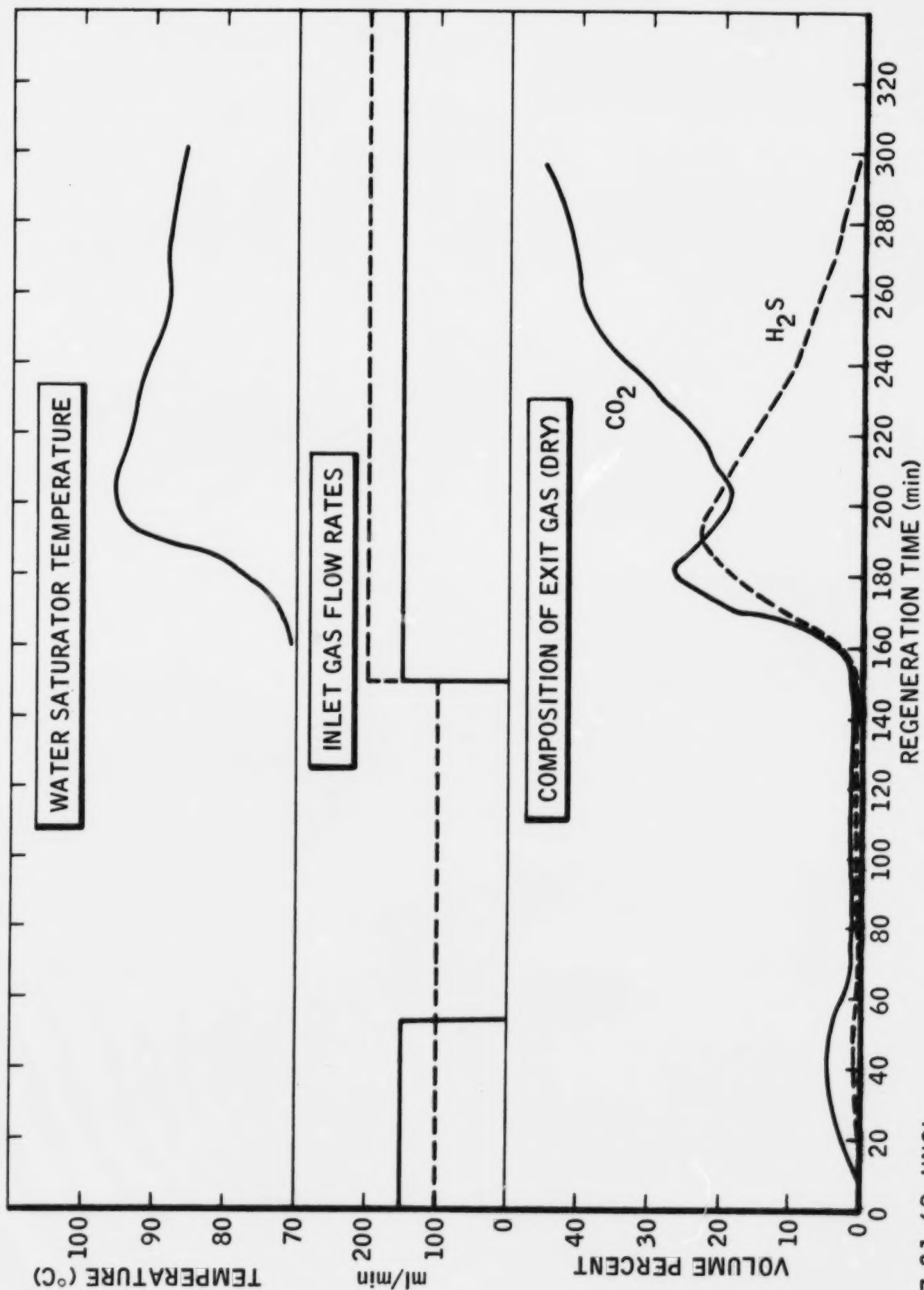


Figure 6. Regeneration of a Pure Melt (Test 2)

7732-4021

7-31-68 UNCL

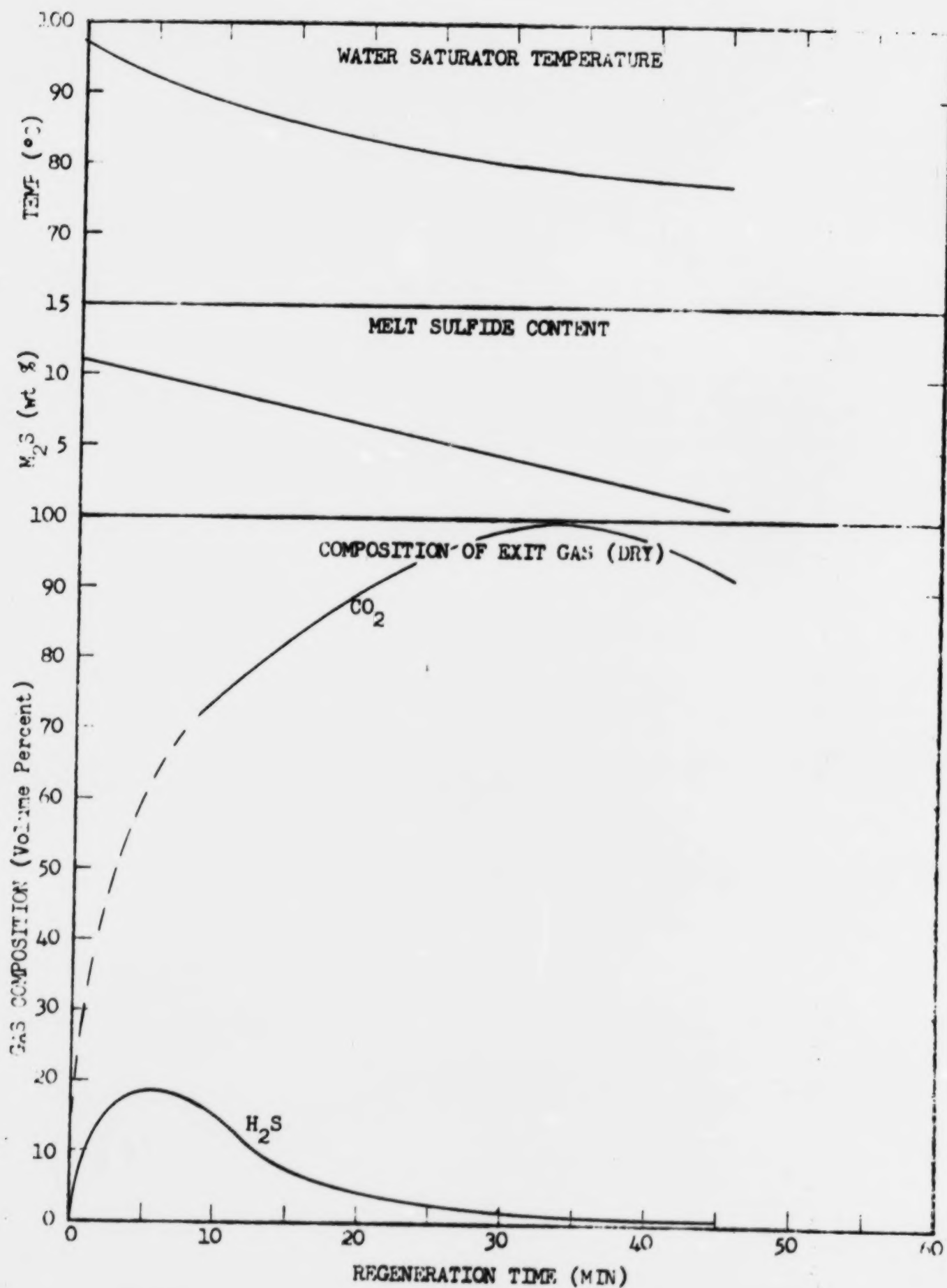
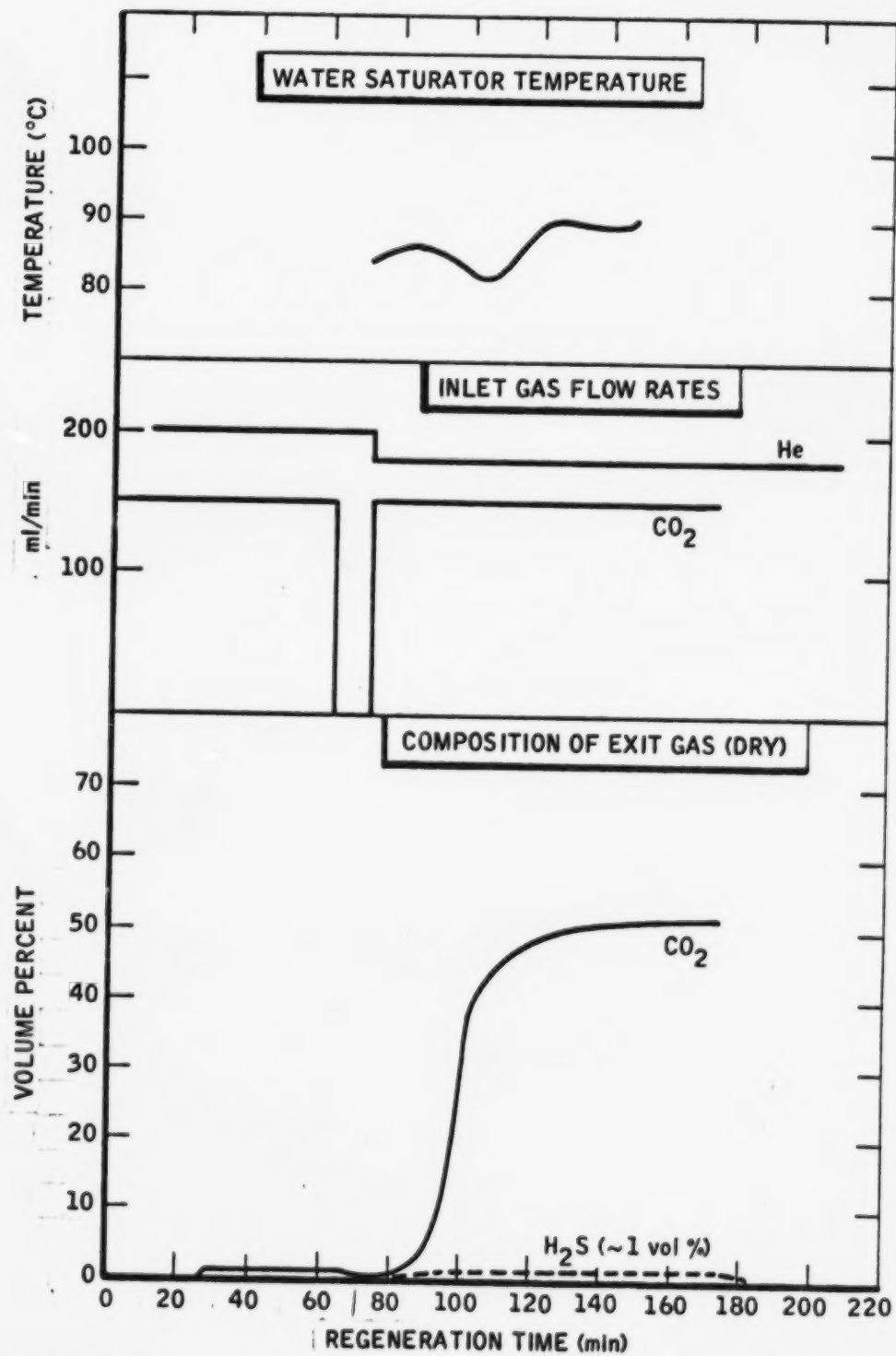


Figure 7. Regeneration of Melt Reduced with Carbon Monoxide (Test 3)



7-31-68 UNCL

7732-4023

Figure 8. Effect of Tin on Regeneration (Test 4)

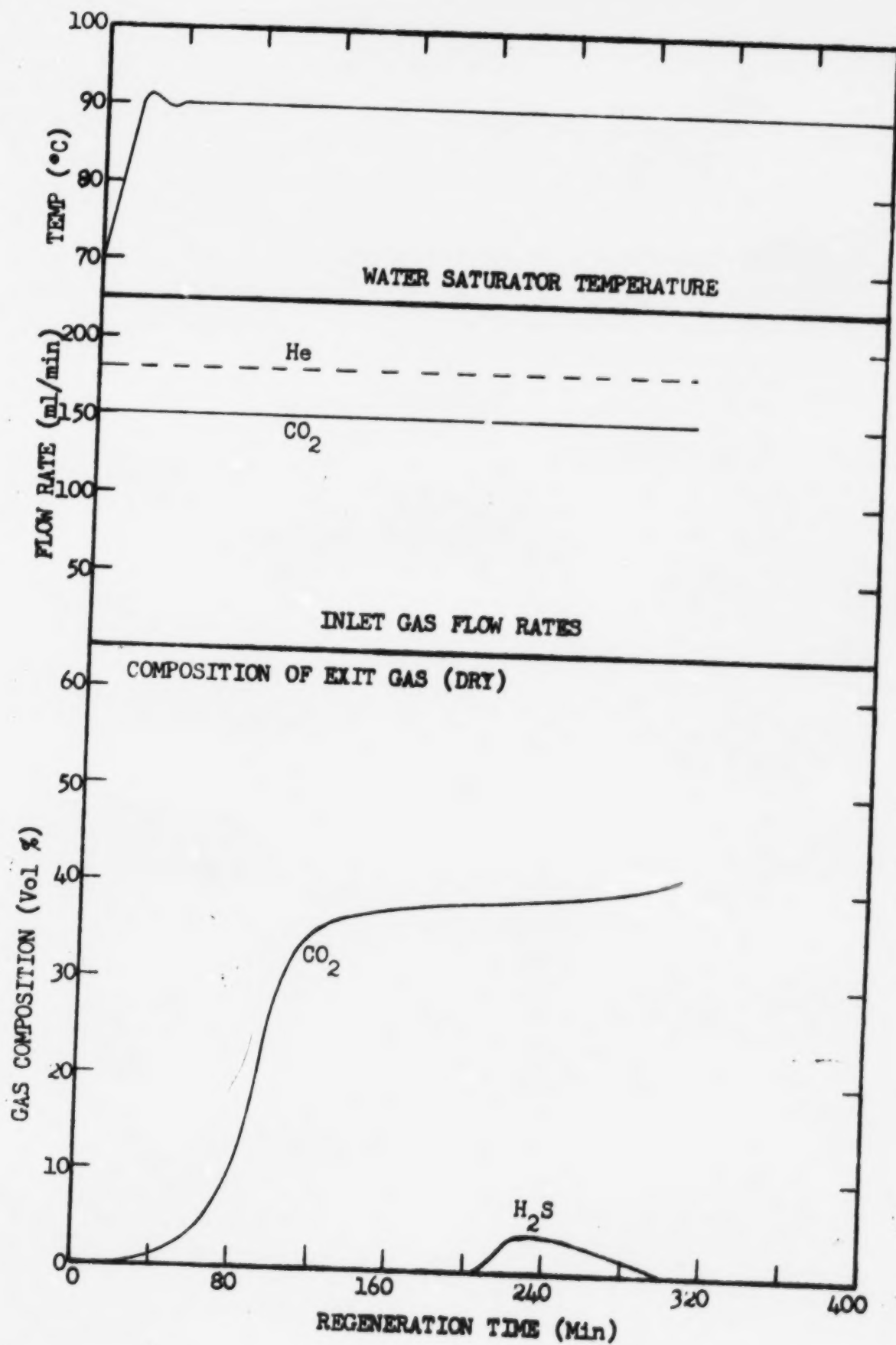


Figure 9. Effect of Germanium on Regeneration (Test 5)

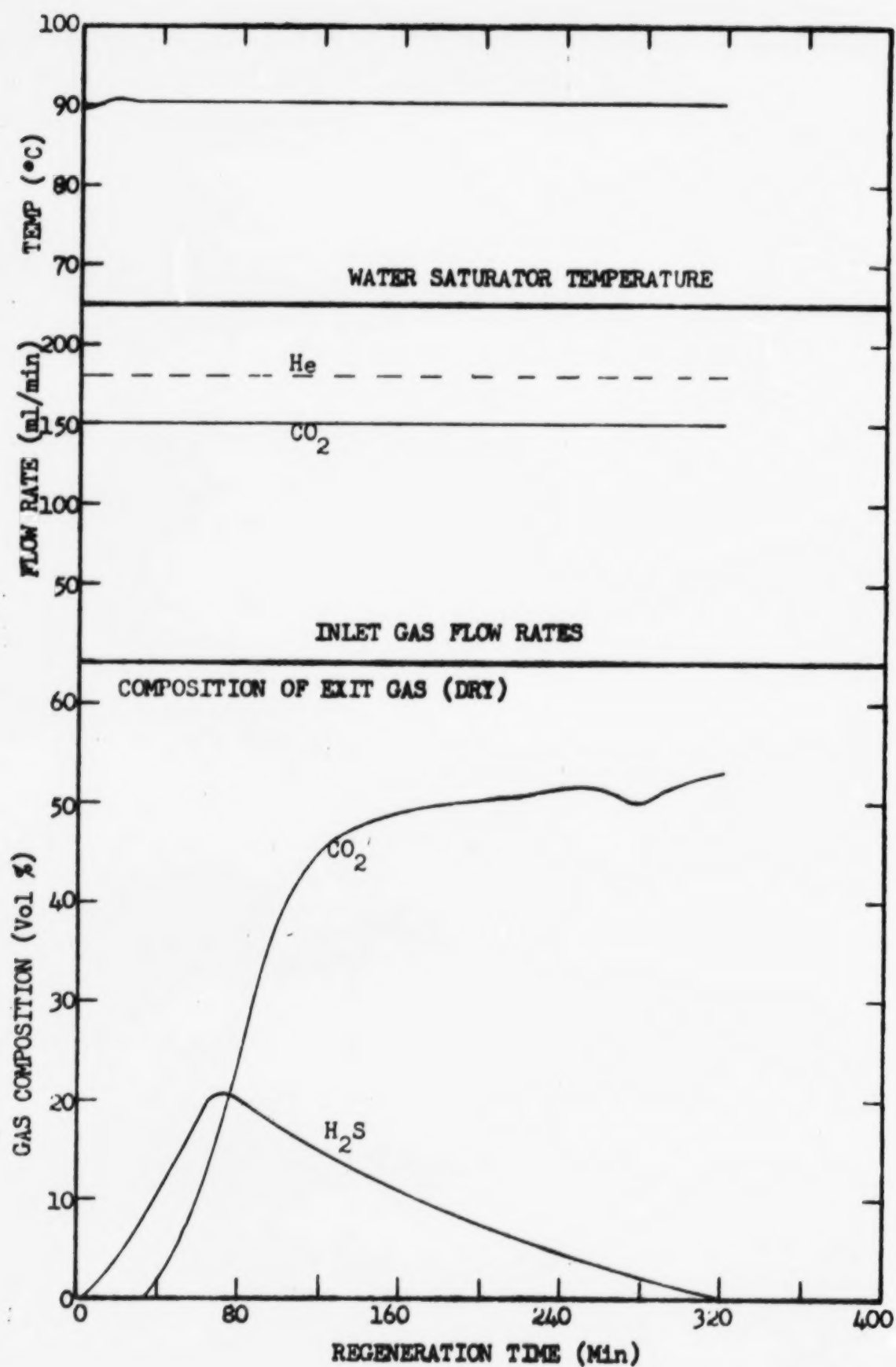


Figure 10. Effect of Molybdenum on Regeneration (Test 6)

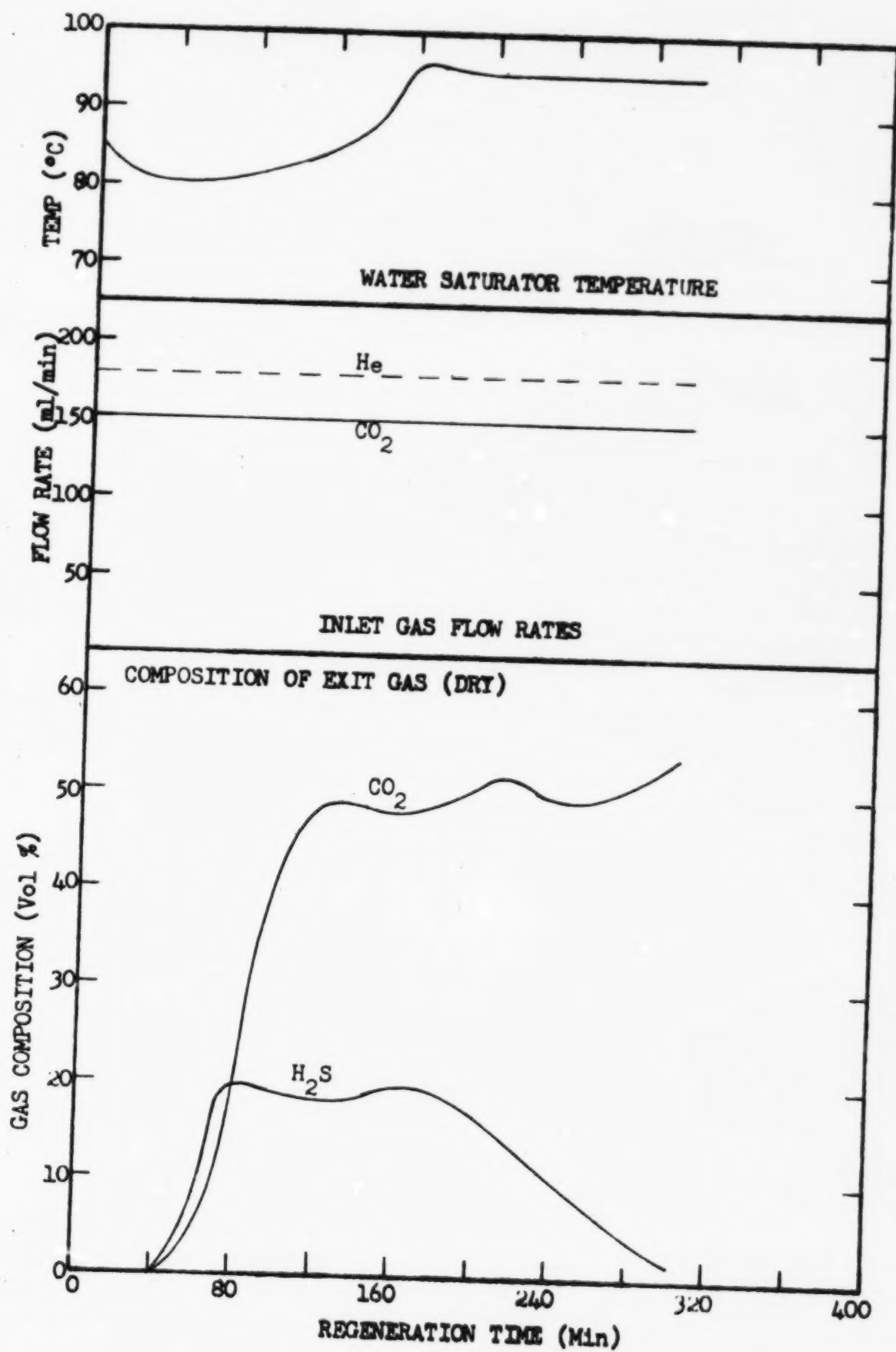


Figure 11. Effect of Vanadium on Regeneration (Test 7)

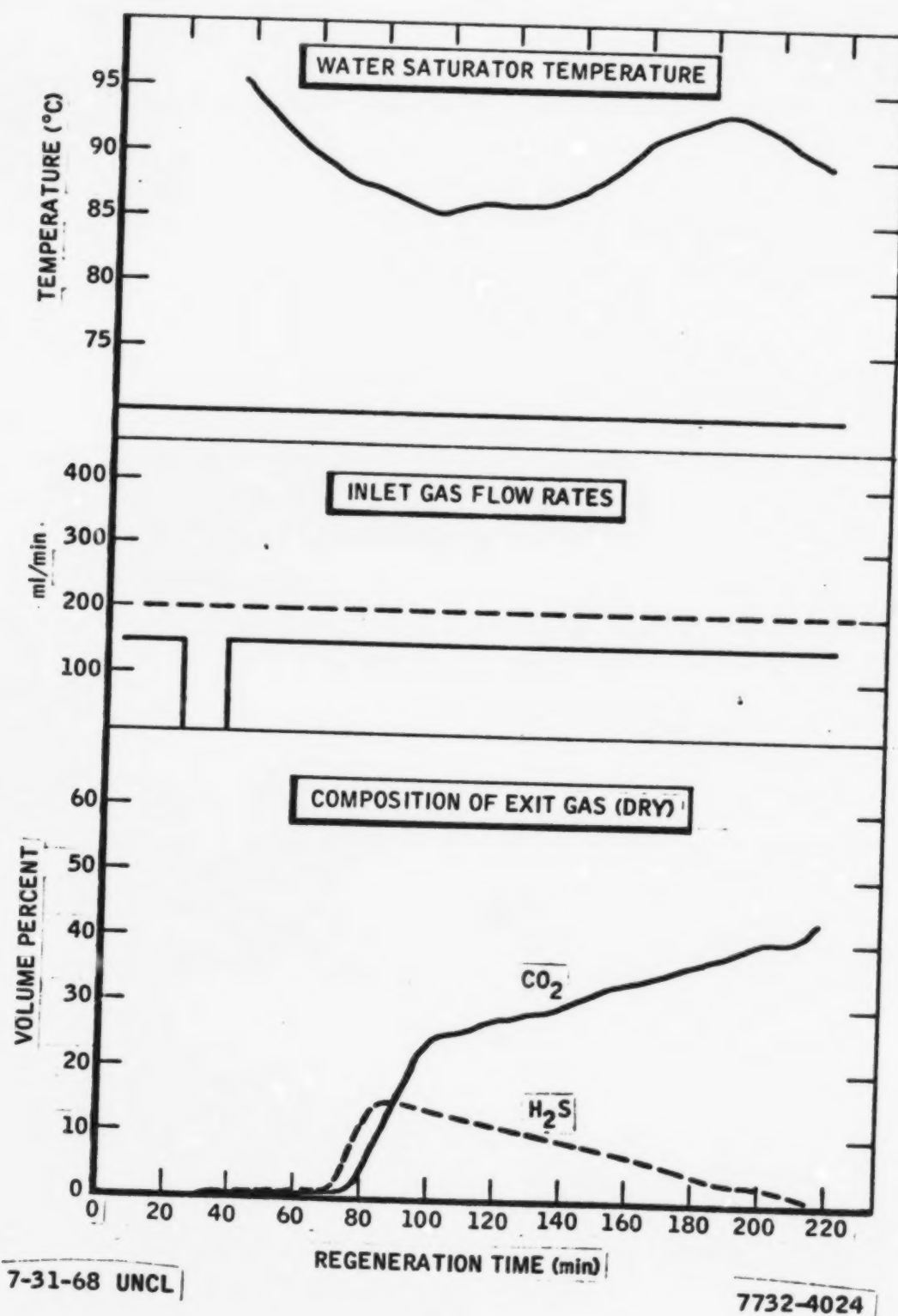


Figure 12. Effect of Iron on Regeneration (Test 8)

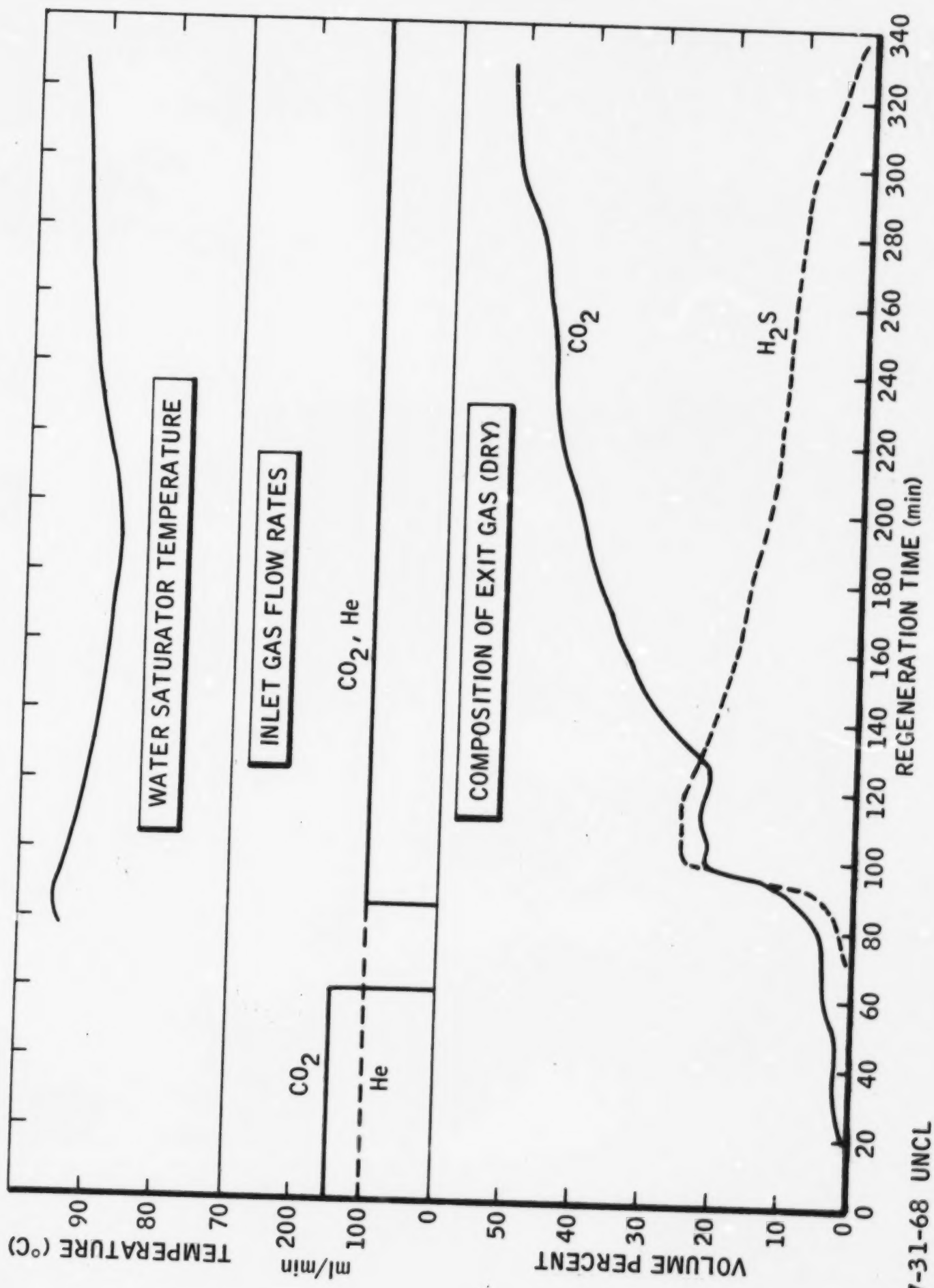
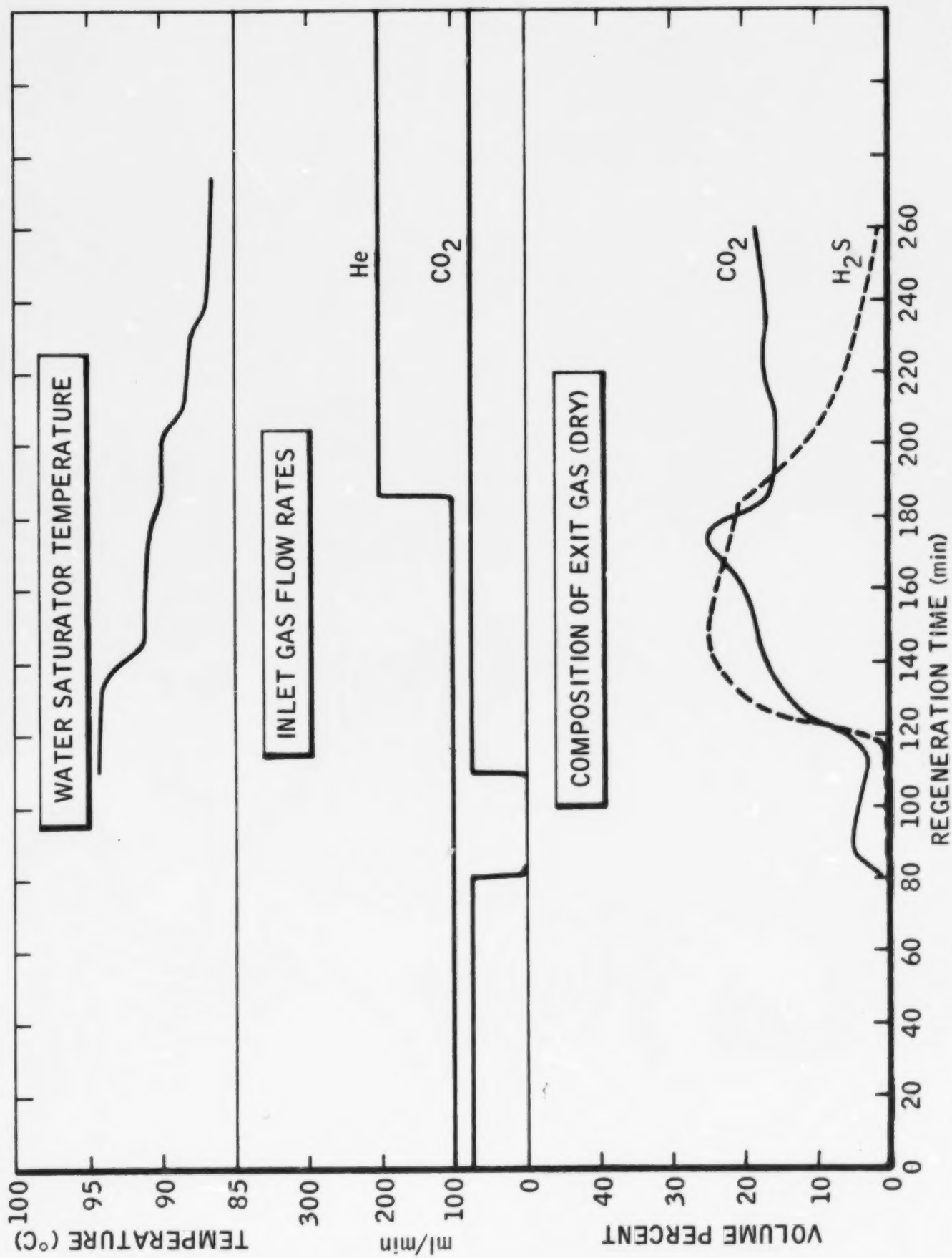


Figure 13. Effect of Iron on Regeneration. Iron Metal Added Prior to Reduction Step (Test 9)

7732-4018

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7-31-68 UNCL

7732-4019

Figure 14. Effect of Iron on Regeneration. Iron Sulfide Added Prior to Reduction Step (Test 10)

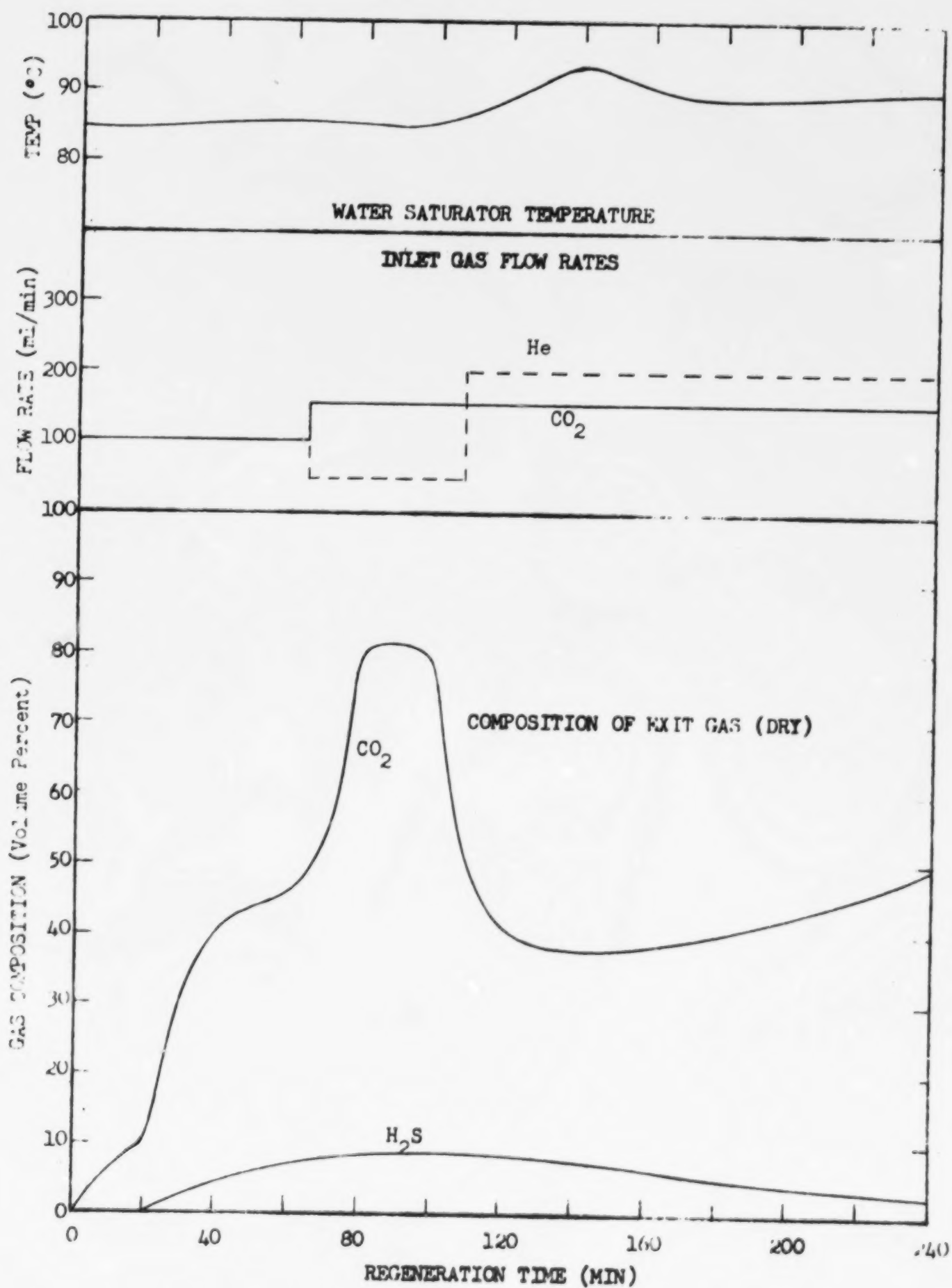


Figure 15. Effect of 30°C Reduction on Regeneration of Iron-Containing Melt (Test 11)

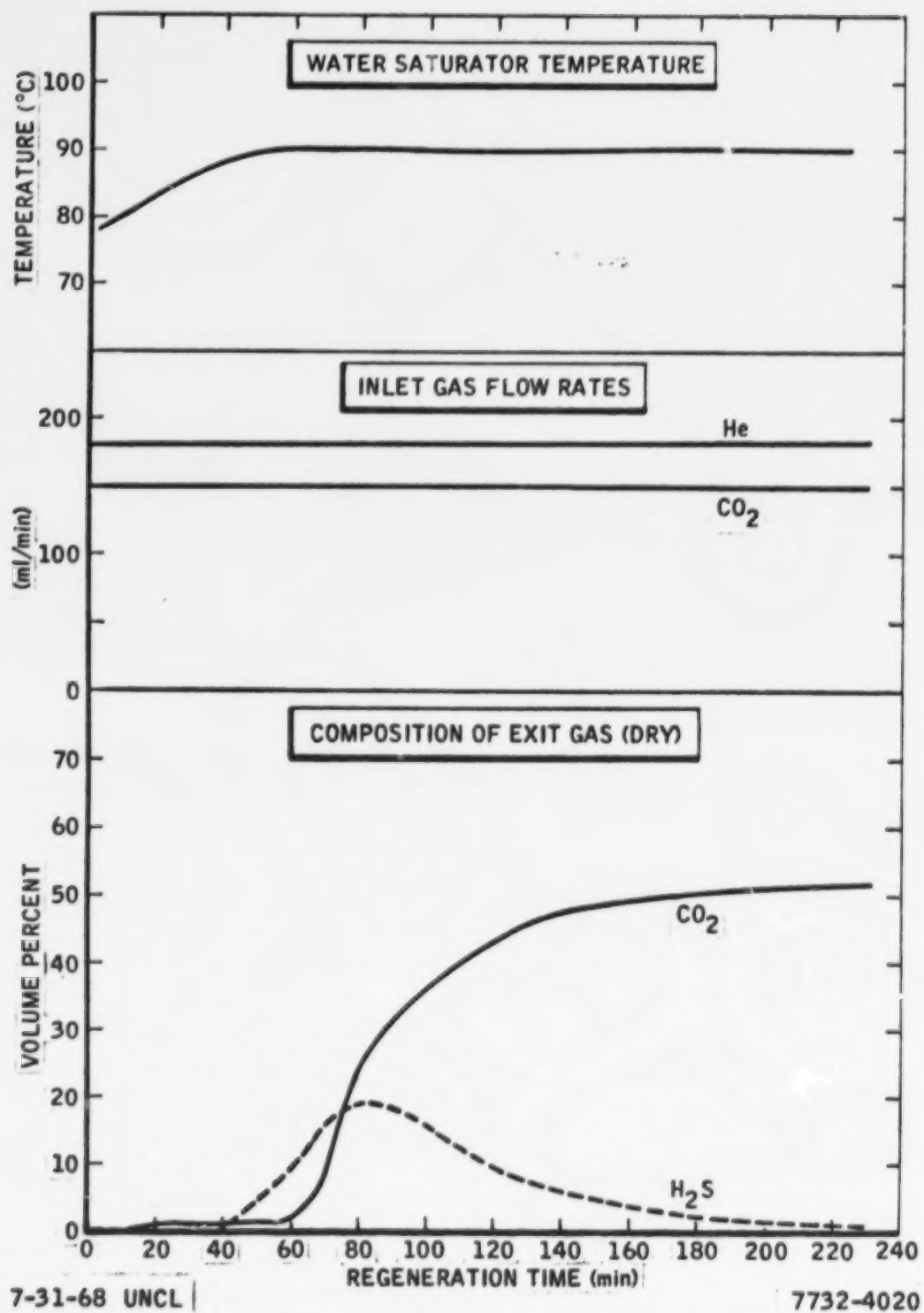


Figure 16. Effect of 700°C Reduction on Regeneration of Iron-Containing Melt (Test 12)

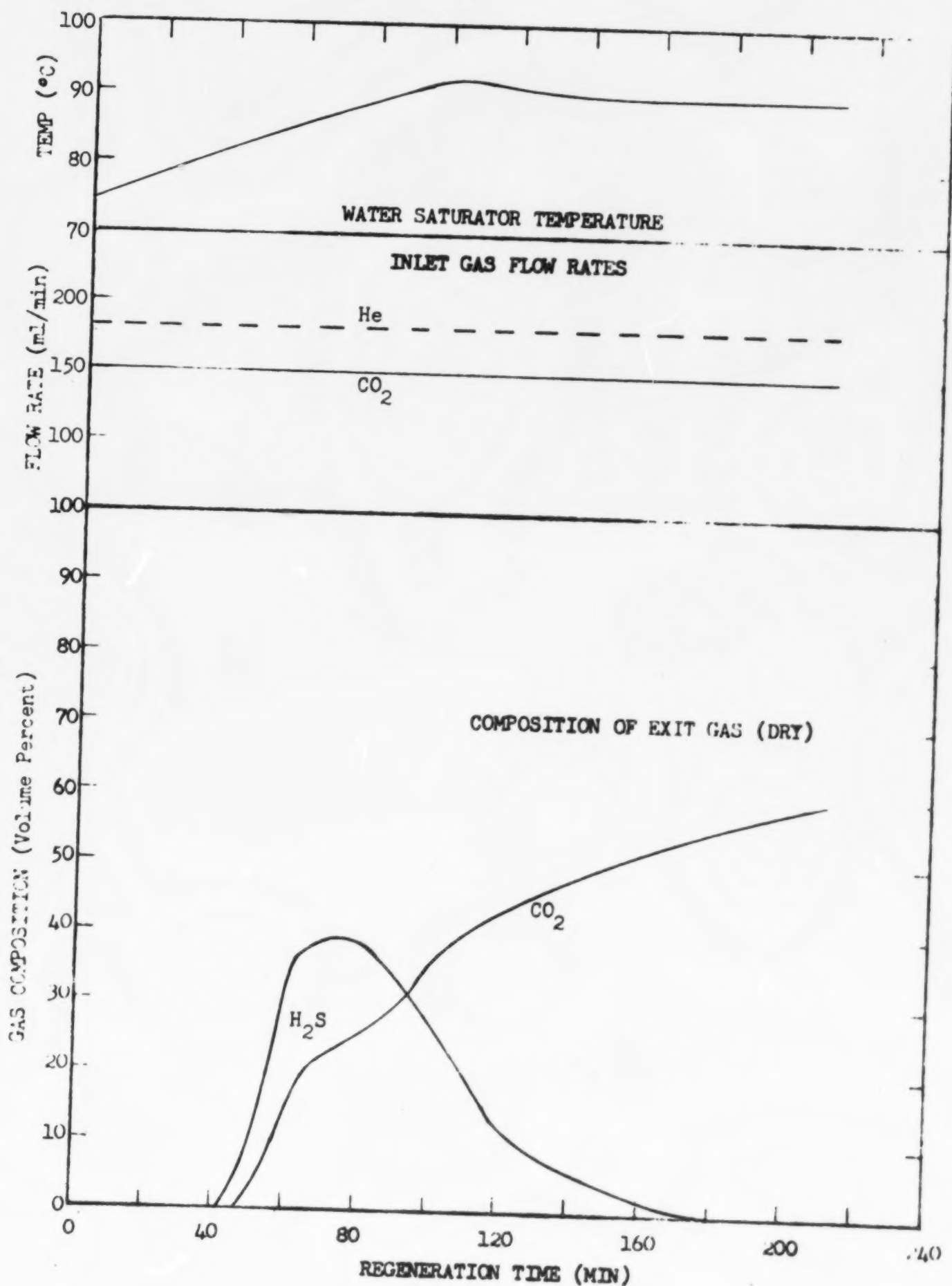


Figure 17. Effect of 5 Atm Hydrogen Reduction on Regeneration of Iron-Containing Melt (Test 13)

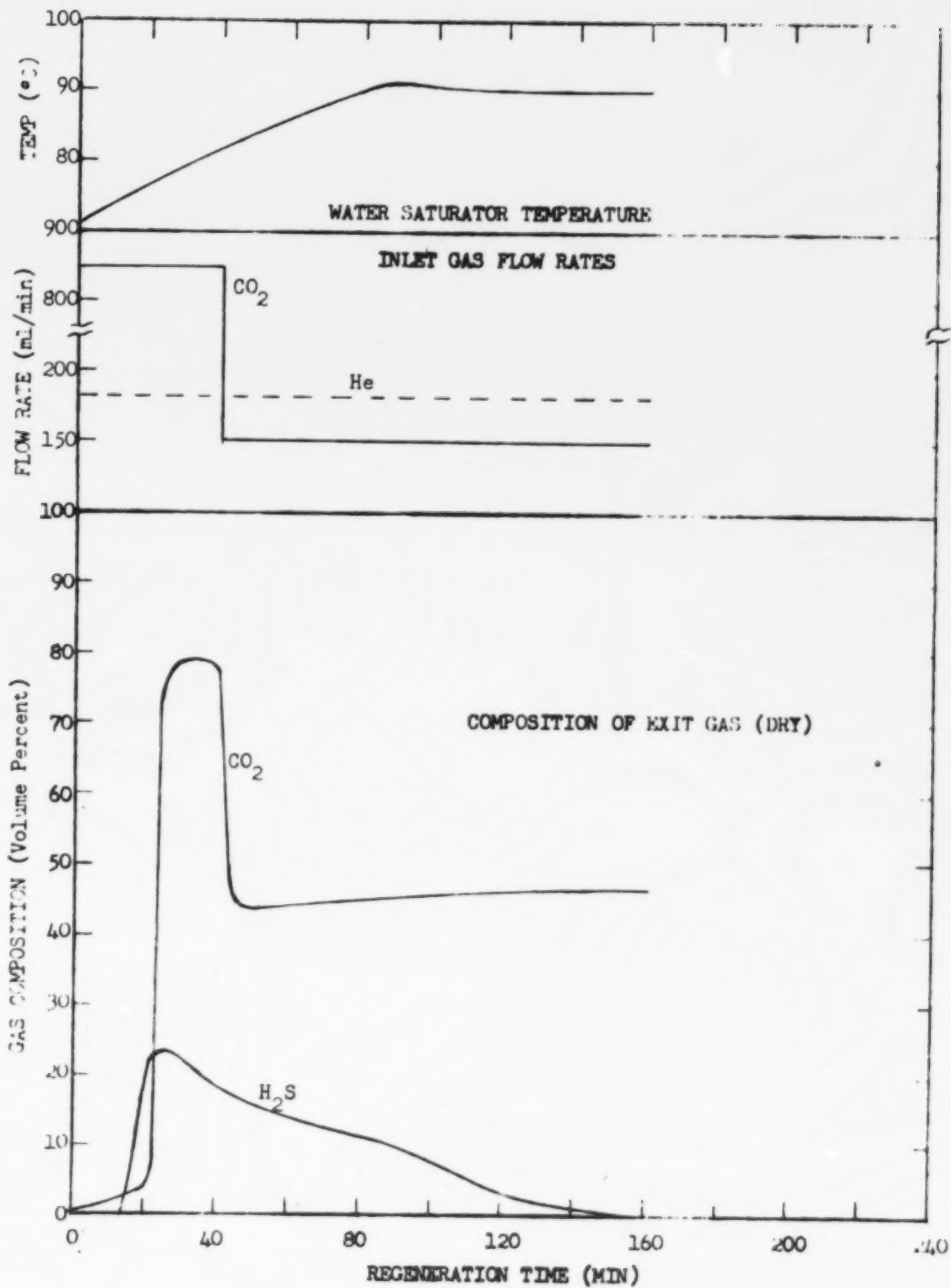


Figure 18. Effect of Wet Hydrogen Reduction on Reduction of Iron-Containing Melt (Test 14)

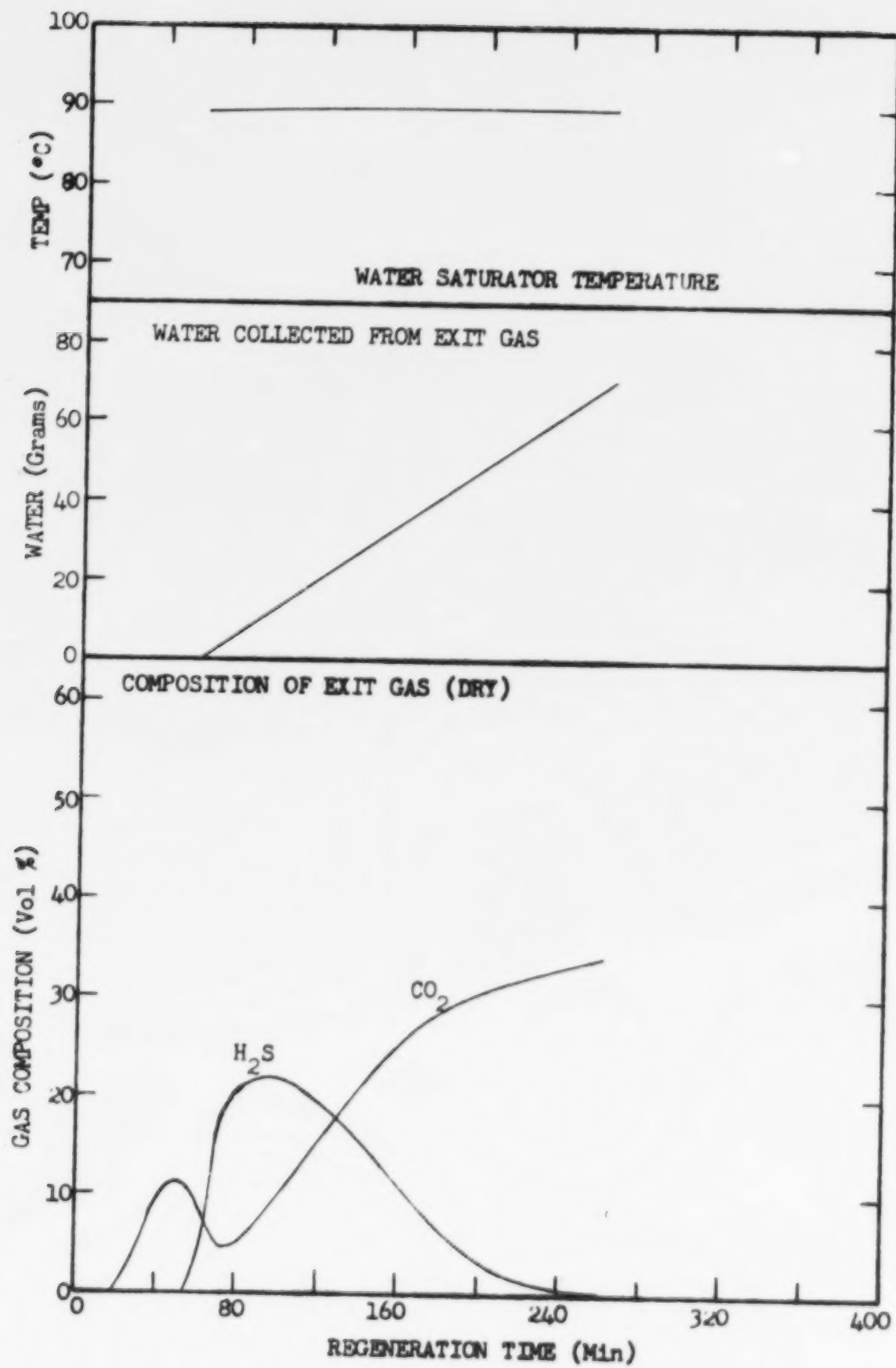


Figure 19. Regeneration at 425°C (Test 15)

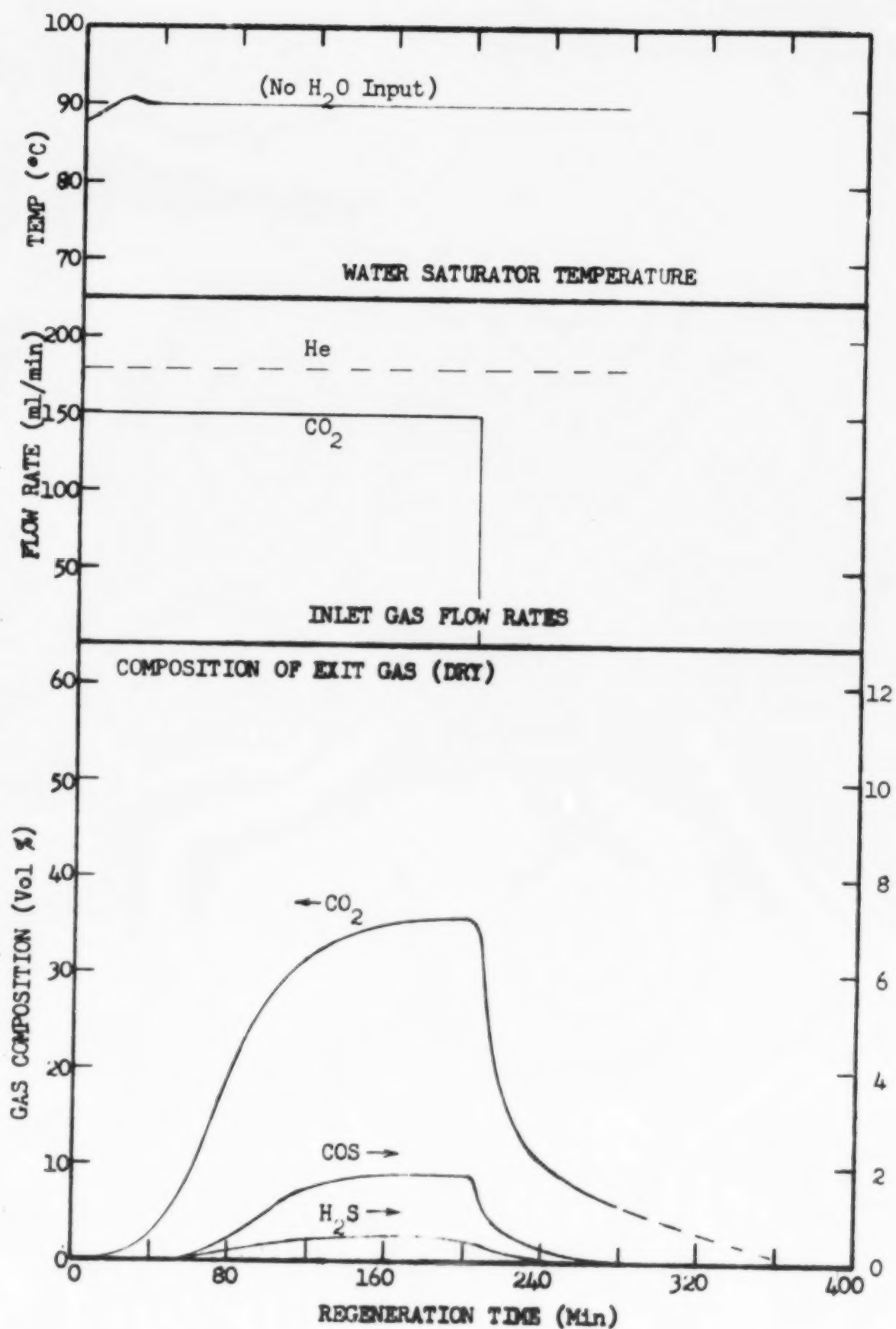


Figure 20a. Effect of Separate Carbon Dioxide and Steam Treatments During Regeneration. Part 1 (Test 16)

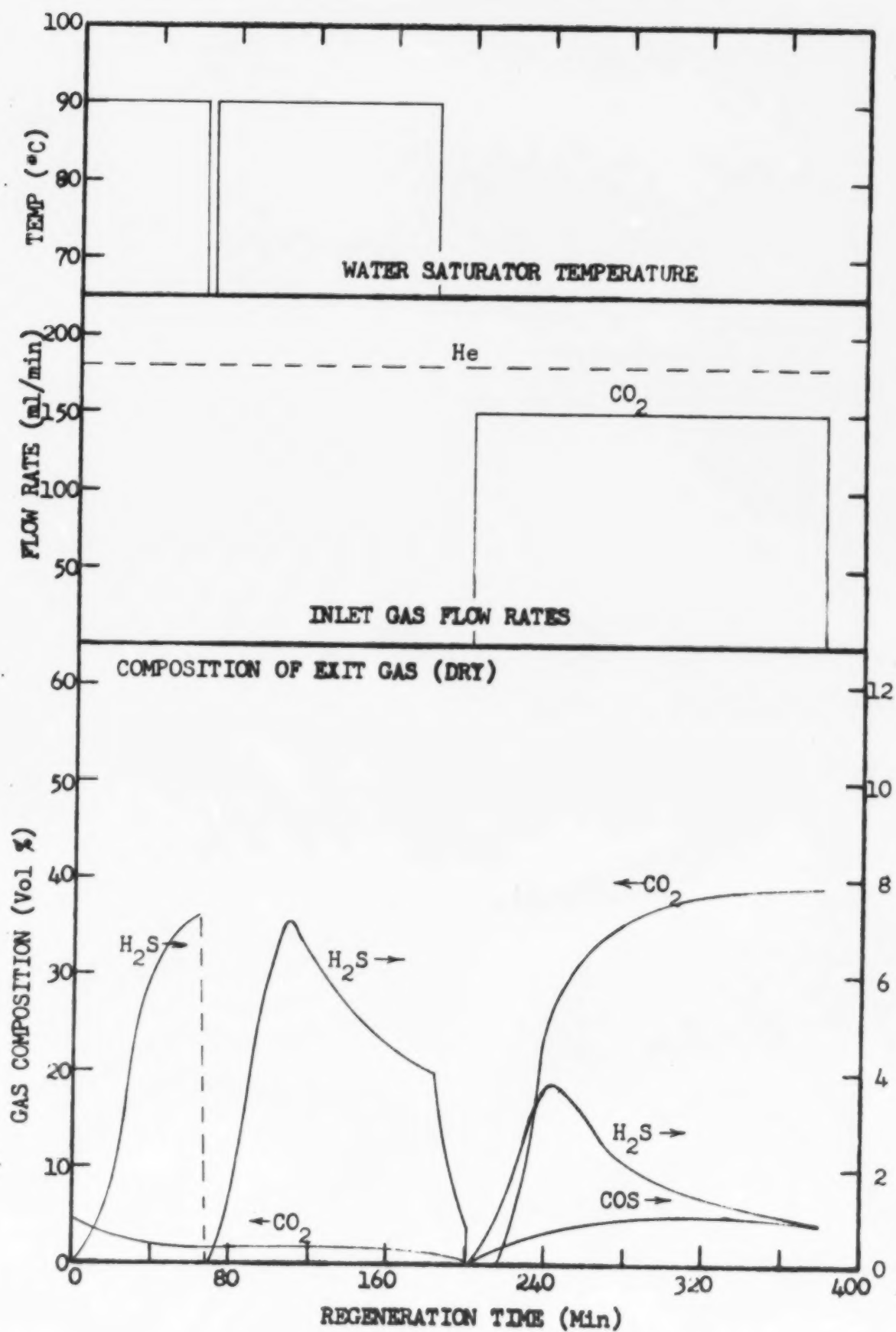


Figure 20b. Effect of Separate Carbon Dioxide and Steam Treatments During Regeneration. Part 2 (Test 16)

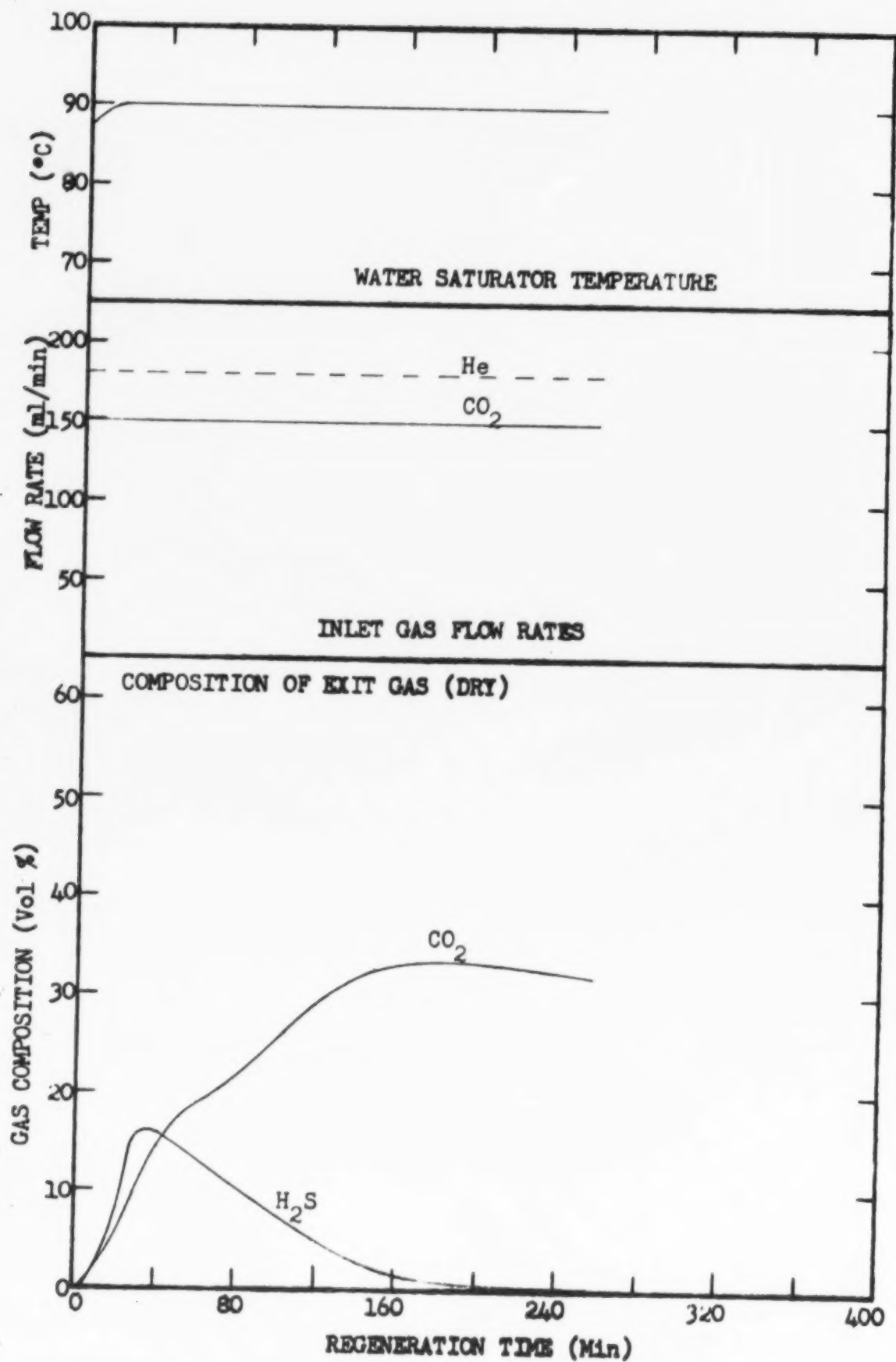


Figure 20c. Effect of Separate Carbon Dioxide and Steam Treatments During Regeneration. Part 3 (Test 16)

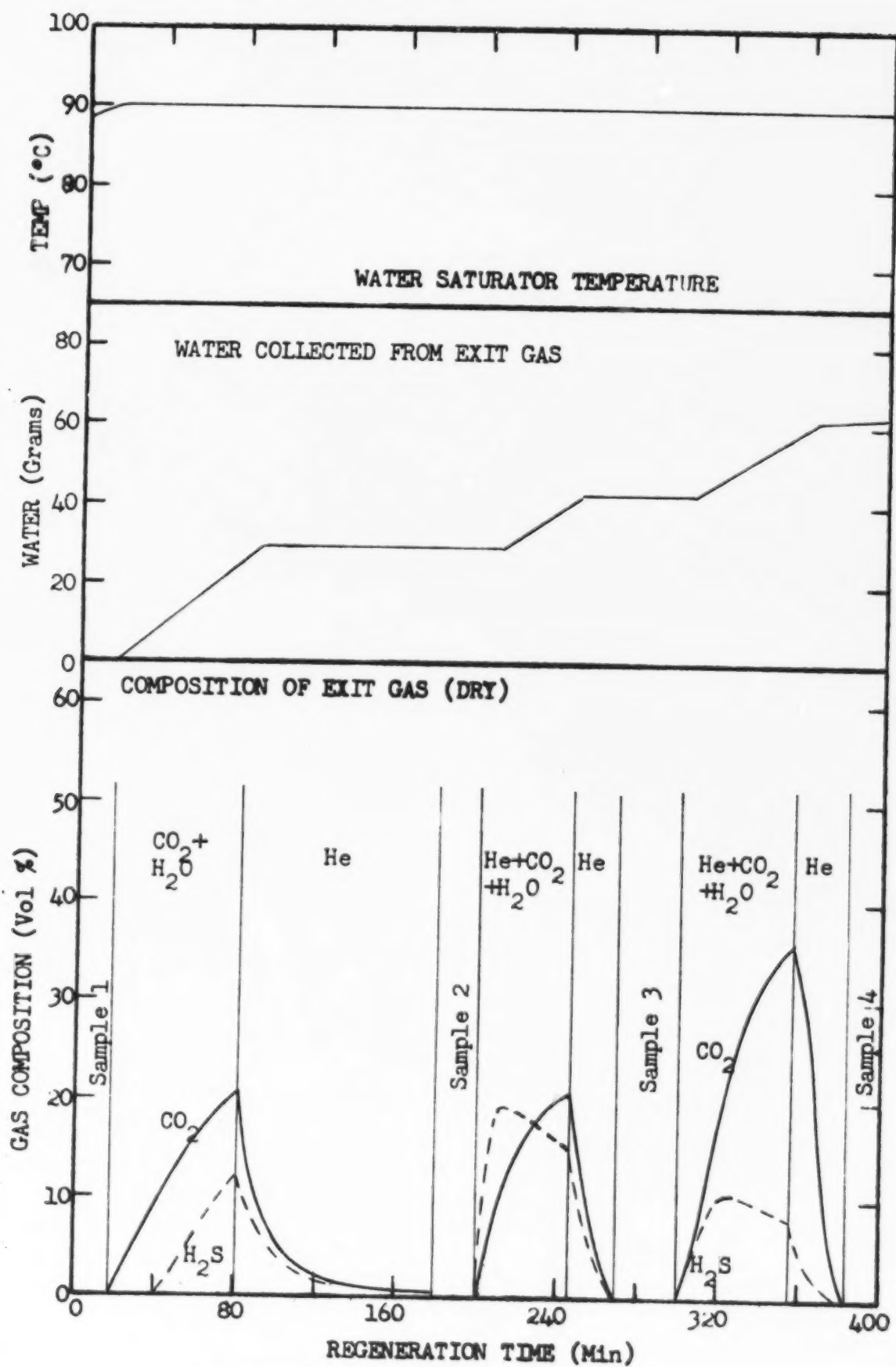


Figure 21. Sampling and Filtration During Regeneration of Iron-Containing Melt (Test 17)

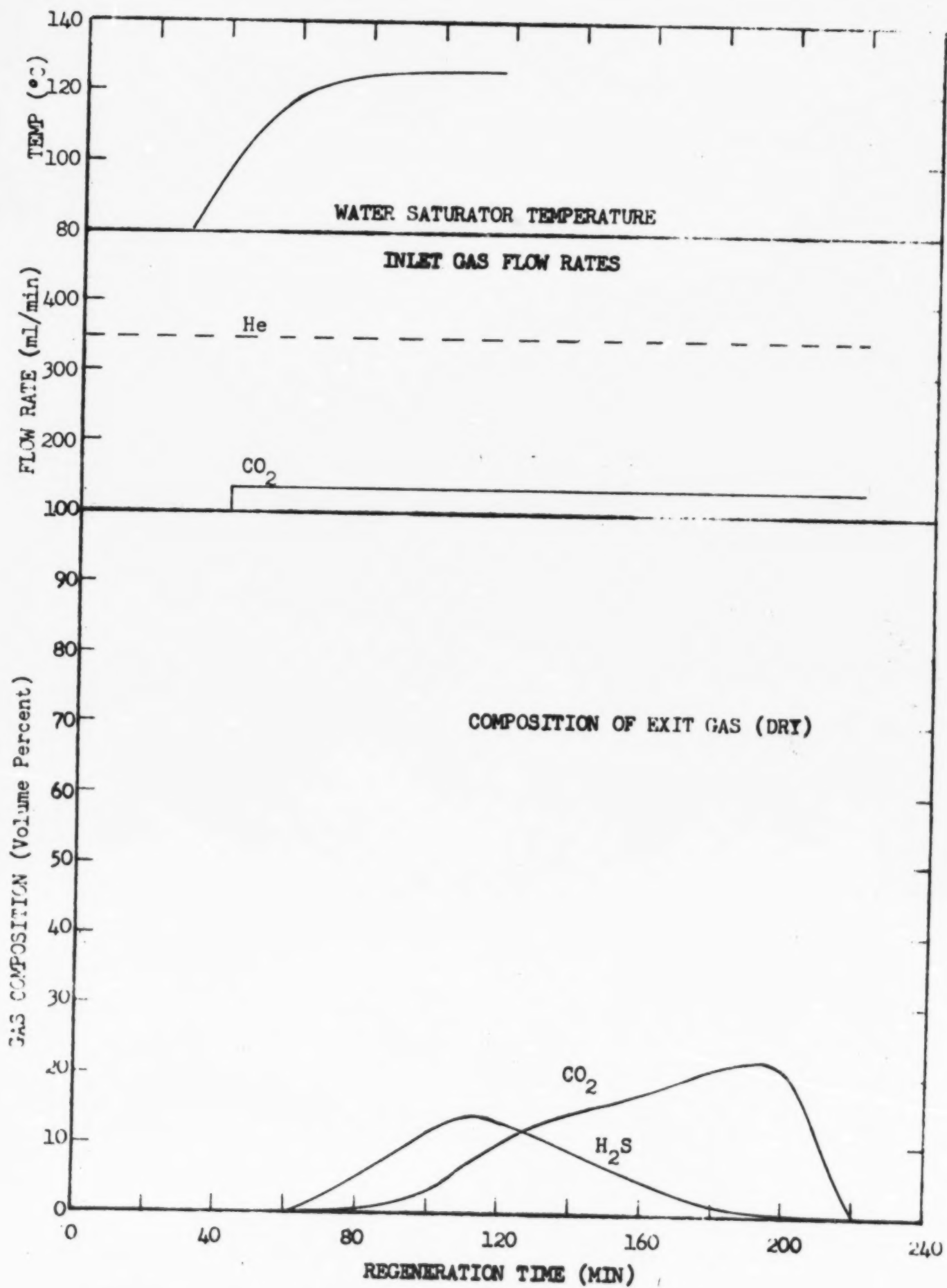


Figure 22. Effect of Higher Pressure During Regeneration (Test 18)

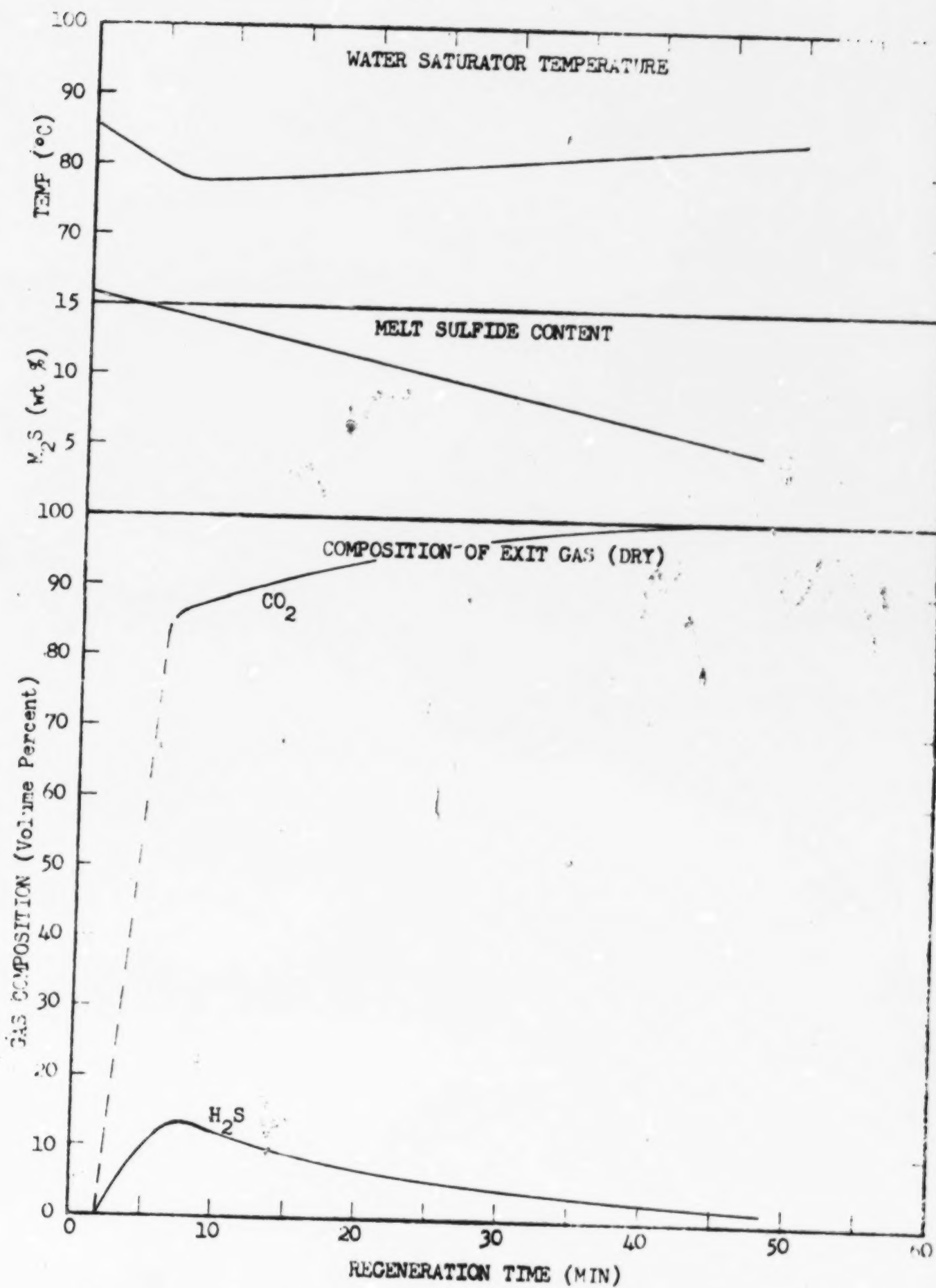


Figure 23. Regeneration of Iron-Containing Melt Reduced with Carbon Monoxide (Test 19)

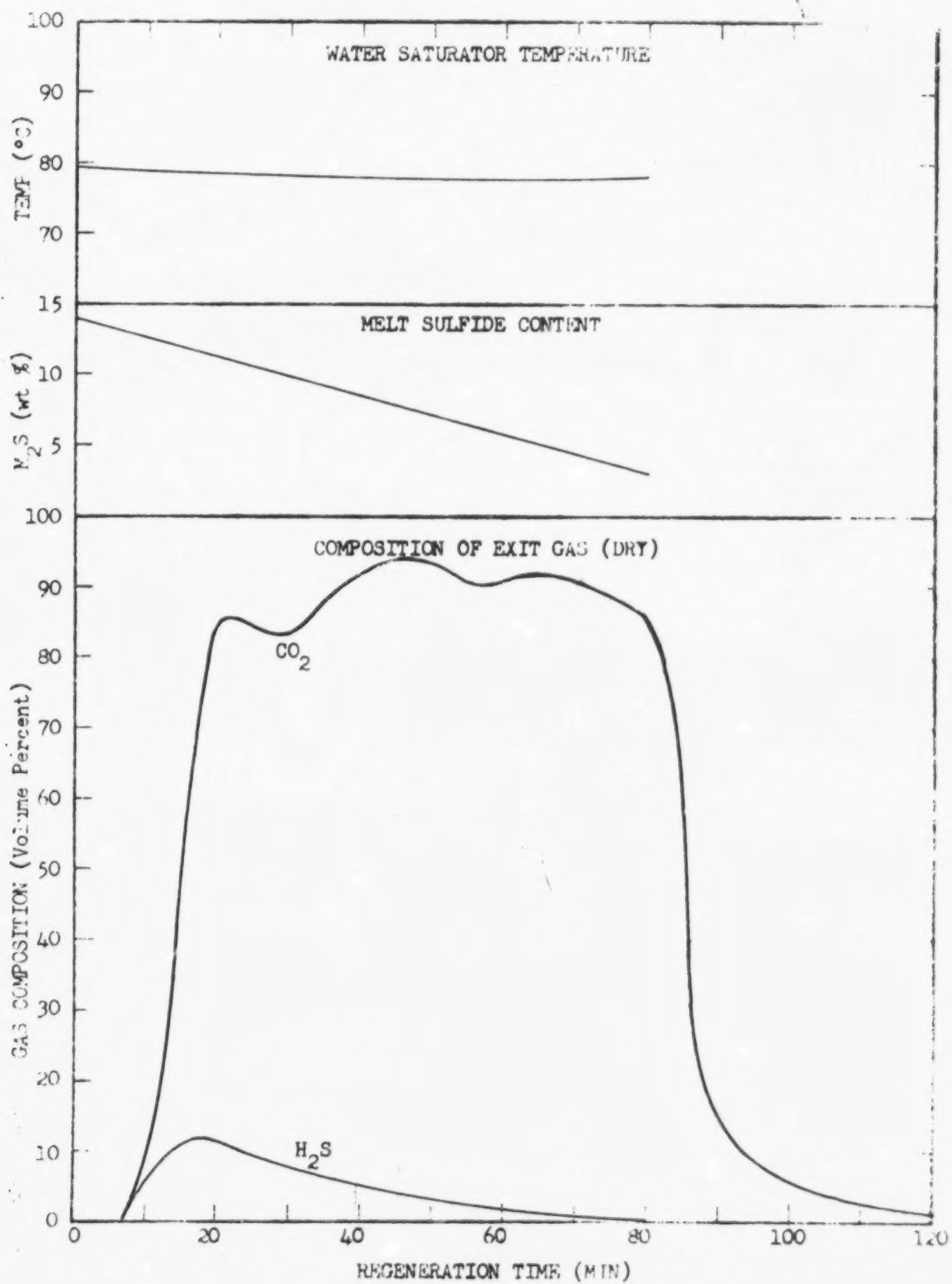


Figure 24. Effect of Calcium on Regeneration (Test 20)

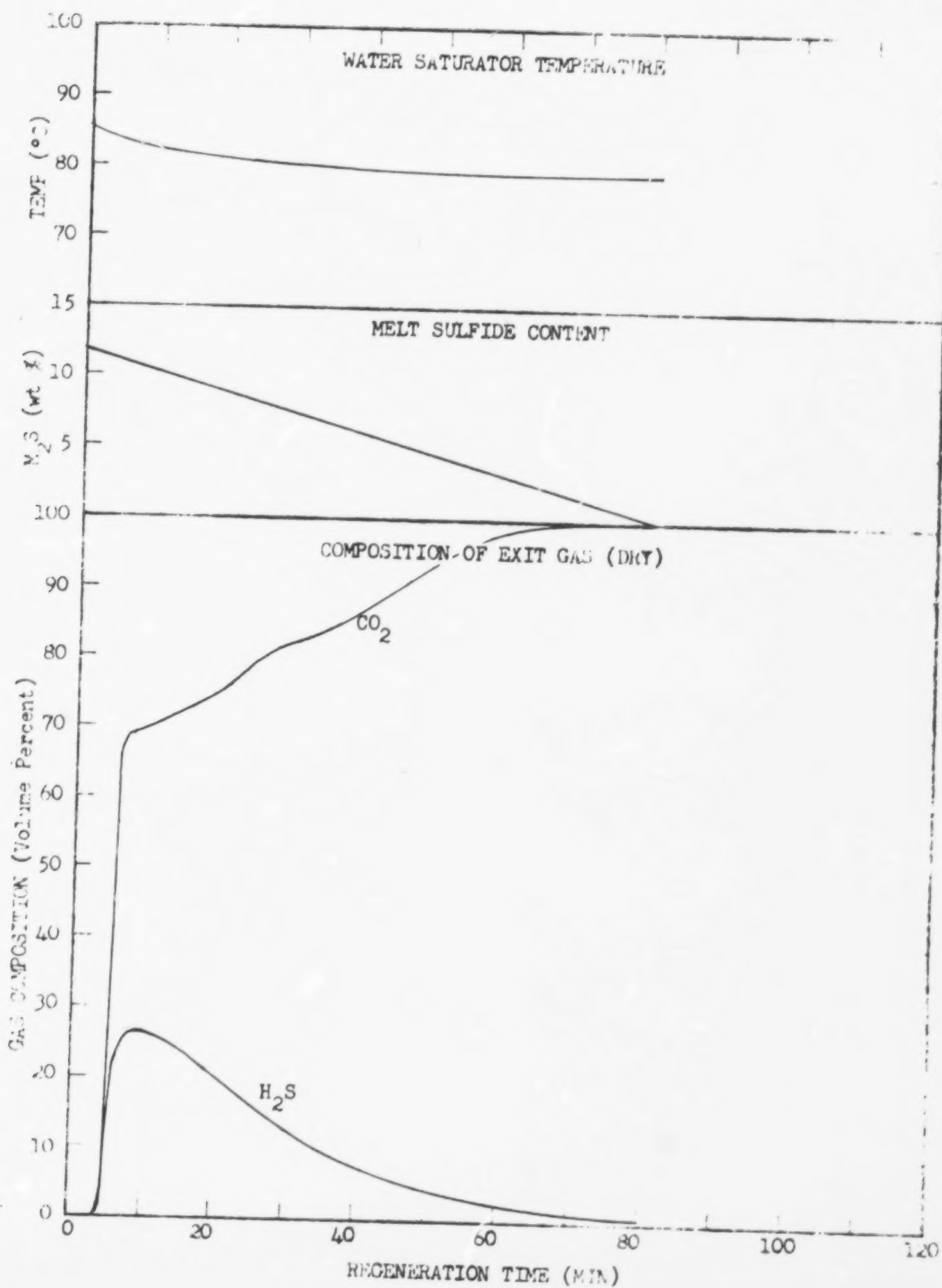


Figure 25. Regeneration of a Melt Containing a Small Amount of Iron at a High Gas Flow Rate (Test 21)

extent during the course of each regeneration, these variables were also plotted against regeneration time.

The figure corresponding to each regeneration test is as follows:

<u>Regeneration Test No.</u>	<u>Figure No.</u>	<u>Regeneration Test No.</u>	<u>Figure No.</u>
1	5	12	16
2	6	13	17
3	7	14	18
4	8	15	19
5	9	16	20a, 20b, 20c
6	10	17	21
7	11	18	22
8	12	19	23
9	13	20	24
10	14	21	25
11	15		

4. Melt Sulfide Contents After Regeneration

The amount of sulfide remaining in the melts after regeneration (Column 7, Table 4) varied from 0.0 to 8.5 weight percent. The results showed that over 90% of the sulfide would be removed from most melts, but that certain metals (e.g., tin, germanium and iron) inhibited the regeneration reaction. Thus, in the molten carbonate process, it will be necessary to keep the concentration of the above metals to a low level. Since iron is the only metal likely to be present in significant amounts (from either fly ash, corrosion or as an added reduction catalyst), the effects of iron in the regeneration step were studied in some detail and are discussed below in parts 6 and 8.

The data in Table 4, Column 7, show that essentially all ($> 90\%$) of the sulfide could be removed from pure salts (Class 1) and from some of the melts belonging to Class 2, namely those containing molybdenum and vanadium. The pure carbonate melts (Test Nos. 1, 2 and 3) contained from 0.0 to 0.9 wt% sulfide after regeneration. The melts containing molybdenum and vanadium contained 0.13 and 0.96 wt% sulfide, respectively. The melts containing tin and germanium (Test Nos. 4 and 5) appeared to contain relatively small amounts of sulfide (2.6 and 0.12 wt%, respectively). However, both tin and germanium interfered with the standard analytical method for determining melt sulfide content. The true sulfide contents of these melts had to be determined by the total sulfur method and the results of those analyses, described in Section III D below, showed that only a small amount ($< 10\%$) of the sulfur had been removed from these melts during the regeneration. The final sulfide contents of the melts containing iron varied considerably, ranging from zero (Test No. 21) to 8.5 wt% (Test No. 12). However, sulfur recovery values based on the amount of hydrogen sulfide collected from the exit gas, showed that no more than 70% of the sulfide could be removed as hydrogen sulfide from melts containing iron in a one-cycle test. The reason for the variation in the final melt sulfide contents (after regeneration of melts containing iron) appeared to be caused by variations in the amount of foaming which occurred during regeneration (discussed below in part 6).

5. Hydrogen Sulfide Content of Exit Gas from Regeneration Tests

Figures 5 to 25 show that the carbon dioxide and hydrogen sulfide contents of the exit gas in most cases rise sharply after a period of time and then the hydrogen sulfide content gradually decreases to a small value while the carbon dioxide content increases to a level corresponding to the inlet

carbon dioxide content. The gradual decrease in the hydrogen sulfide content shows the effect of the decreasing melt sulfide concentration on the equilibrium concentration of hydrogen sulfide in the gas phase. A detailed analysis of the equilibrium involved between the melt and gas phase is described in part D, section IV. It is apparent that in order to maintain a relatively high (> 20 vol%) and constant hydrogen sulfide content in the exit gas in the process, it will be necessary to carry out the regeneration step in a continuous countercurrent manner.

The maximum hydrogen sulfide contents (18-28 vol%) of the exit gases shown in Figures 5-7 for the pure sulfide melts were appreciably greater than they were for the sulfide melts which contained tin (Figure 8) and germanium (Figure 9) (3 and 4 vol% hydrogen sulfide, respectively). This indicates that both of these metals tie up an appreciable amount of the sulfur in a less reactive form. Molybdenum and vanadium (Figures 10 and 11) have a similar but less pronounced effect on reducing the hydrogen sulfide content of the exit gas.

The exit gas composition during the regeneration tests on sulfide melts containing iron are shown in Figures 12 to 25. Figures 12, 13 and 14 show that the iron-containing melts used in Tests 8, 9 and 10 behave similarly (with respect to the hydrogen sulfide content of the off gas) to the pure carbonate melts on regeneration, even though iron ties up some of the sulfide in a form which cannot be regenerated. This indicates that iron ties up only a fraction of the sulfide in an unreactive form but left the remaining sulfide at its normal activity. This was in contrast to the effect of the other metal impurities, especially tin and germanium, which appeared to reduce the total sulfide activity to a lower value.

6. Regeneration and Foaming of Reduced Melts Containing Iron

Since iron is an effective catalyst for the hydrogen reduction of sulfate melts, a number of regeneration tests were carried out on reduced sulfide melts containing iron. In general, the melt volumes (Column 5, Table 4) decreased much more during regeneration of the melts containing iron than they did in the melts which contained no iron (Column 5, Table 4). Most of this decrease was found to be due to foaming, which occurred during the regeneration of melts containing iron. This foaming resulted in the deposition of a substantial portion of the melt on the reactor walls about one inch above the melt line. This deposit collected as a semi-solid deposit which would not flow back into the melt after it had been deposited. The amount of foaming varied to some extent, depending upon the reduction and regeneration conditions, and as a consequence the final sulfide content of the melt after regeneration (Column 7, Table 4) varied depending upon the extent of foaming. If an appreciable amount of foaming occurred as in Test No. 8, Table 4, then the melt sulfide content was found to be low ($< 0.2 \text{ wt\% } \text{M}_2\text{S}$) even though only 60-70% of the sulfide was removed as hydrogen sulfide. The remaining sulfide was found in the iron-sulfide-rich deposit which formed above the melt line (see part 2f, Section III for the results of analysis of froth deposits from regeneration of sulfide melts). The effects of changes in reduction and regeneration conditions on the foaming tendency of iron-containing melts is discussed in Section IV. The analysis of the data indicated that the reduction temperature and pressure and the regeneration temperature and pressure as well as the kind of reducing agent, affect the tendency of a melt to foam during regeneration.

7. Regeneration at Different Temperatures

Figure 15 showed that the hydrogen sulfide content of the exit gas was appreciably reduced when the melt was regenerated at a higher temperature (600°C instead of 500°C) while the data plotted in Figure 19 for a regeneration test at 425°C show that the hydrogen sulfide content was considerably higher than at 500°C. The inspection of plots of this type can only be used for qualitative conclusions since all of the factors including initial melt sulfide content, water saturator temperature, and inlet gas carbon dioxide content have to be considered for an exact comparison. These factors were taken into account for a number of tests as described in a later section (Section IV). It is apparent, however, that the equilibrium of the regeneration reaction is more favorable at the lower temperatures.

8. Solubility of Iron During Regeneration

During the regeneration of a melt containing iron (regeneration test No. 17), melt samples were taken at intervals during the regeneration reaction. Two melt samples were taken at each interval, one filtered and one unfiltered. The results, shown in Table 5, indicate that the solubility of iron (column 7) decreased greatly as the regeneration neared completion. The final sample contained 0.01 wt% iron, which showed that iron can be removed almost quantitatively from regenerated melts by filtration. A comparison of the total sulfide and soluble sulfide content of the melt also showed that an appreciable amount of the sulfide becomes insoluble during the reaction. The data indicate that the sulfide precipitated along with the iron in the form of an insoluble iron sulfide compound.

TABLE 5
Composition of Filtered and Unfiltered Melt
Samples During Regeneration Test 24

Melt Description and Regeneration Stages	Melt Condition		Melt Composition (wt %)			
	Temp (°C)	Sample Method ^a	M ₂ CO ₃	M ₂ S	M ₂ SO ₄	Fe
Prior to Reduction	600	U	62.9	9.1	24.1	(2.4) ^b
After Reduction	600	U	68.2	29.3	3.9	(2.4)
Cooled to 500°C	500	U	66.8	23.7	3.2	2.46
	500	F	71.5	25.4	4.6	2.36
Regenerated with CO ₂ and H ₂ O for 82 min	490	U	77.6	19.2	4.1	3.2
	490	F	85.5	12.3	5.3	0.74
Regenerated for 133 min	490	U	84.4	8.6	4.6	2.66
	490	F	88.9	2.6	5.4	0.12
Regenerated for 189 min	492	U	84.7	7.1	5.2	2.38
	492	F	93.1	0.2	5.4	0.03
Regenerated for 295 min (completed)	493	U	80.7	5.4	4.8	2.60
	493	F	92.1	0.0	4.9	0.01

^a U = unfiltered; F = melt filtered through 35 μ pore size sintered stainless steel filter.

^b Nominal iron concentration given in parenthesis.

9. Retention of Carbon Dioxide by Sulfide Melts

The plots of exit gas composition vs. regeneration time shown in Figures 5, 6, 8, 9, 10 and 11 show that the carbon dioxide content of the exit gas remained at a low value for a longer time than expected, for the system where the gas holdup time was approximately 5-10 minutes at inlet gas feed rates of 300-400 ml/min. The carbon dioxide content remained at a low level for 30 to 60 minutes and then began to rise. This retention of carbon dioxide was found to be due to a side reaction of carbon dioxide with sulfide; this reaction was investigated in more detail and the results are described in a later section (Section III, part 6F). Figure 7 shows the data from regeneration test no. 3, in which a higher carbon dioxide feed rate was used. This melt was prepared by reducing a sulfate-bearing melt with carbon monoxide. There appeared to be a smaller amount of holdup of carbon dioxide by this sulfide melt. This probably resulted from the fact that the melt was reduced with carbon monoxide, with a portion of the carbon dioxide generated during the reduction being retained in the melt.

B. BUBBLE-THROUGH REGENERATION TESTS OF SYNTHETIC SULFIDE-BEARING MELTS

1. Purpose

The purpose in studying the regeneration reaction with synthetic sulfide melts was initially to determine if there were any substantial differences between synthetic sulfide melts prepared by different methods and sulfide melts prepared by a reduction process. Additional regeneration tests were carried out on synthetic melts to study the effects of pressure and contact time on the regeneration reaction.

2. Preparation of Synthetic Sulfide-Bearing Melts

Two methods were used to prepare synthetic sulfide-bearing melts. In the first method, hydrogen sulfide was bubbled through a carbonate melt containing sodium hydroxide. The second method used to prepare synthetic sulfide melts consisted of adding the desired amounts of sodium sulfide, lithium carbonate and potassium carbonate to a eutectic carbonate melt.

3. Organization of Data from Regeneration Tests on Synthetic Sulfide Melts

Table 6 lists the regeneration test conditions on synthetic sulfide-bearing melts. Columns 1 and 2 give the regeneration test number and the method used to prepare the sulfide melt. Columns 3, 4, 5, 6 and 7 give the regeneration test conditions including the system pressure, the carbon dioxide and helium flow rate, the water saturator temperature and the melt temperature. Column 8 gives the major variable change for the test. Data for the regeneration of the synthetic sulfide melts are summarized in Table 7. Columns 2-5 give the condition of the melt prior to withdrawing a melt sample for analysis. These include the melt temperature, the duration and type of treatment completed, and the melt volume. Columns 6, 7 and 8 give the initial weight percentages of the carbonate, sulfide and sulfate in the melt sample.

The data recorded during the regeneration process were feed gas flow rates, water saturator temperature and the composition (carbon dioxide and hydrogen sulfide contents) of the dry exit gas. Figures 26 to 35 show this data plotted versus time for each of the regeneration tests in Table 6.

4. Regeneration of a Sulfide Melt Made by Neutralization of NaOH with H_2S in Molten Carbonate

The melt for regeneration test 22 was prepared by neutralization of sodium hydroxide with hydrogen sulfide in molten carbonate solvent. The

TABLE 6

Bubble-Through Regeneration Test Conditions on Synthetic Sulfide Melts

Expt. #	Preparation of Sulfide Melt	Regeneration Conditions				Melt Temp. °C	Remarks	Fig. No.
		Total Pressure (atm)	CO ₂ ml/min	H ₂ O Sat. Temp., °C	He ml/min			
22	NaOH + H ₂ S in Molten Carbonate	1	1000	60-98	0	500	Sulfide melt prepared by neutralization of NaOH with H ₂ S in molten carbonate.	26
23	Addition of Na ₂ S, Li ₂ CO ₃ , K ₂ CO ₃ to a regenerated melt containing 2 wt% iron	(3)	360	70-120	500	500	Synthetic melt containing iron.	27
24	Addition of Na ₂ S, Li ₂ CO ₃ , K ₂ CO ₃ to M ₂ CO ₃	4.9	400	127-139	0	500	High pressure during regeneration.	28
25	"	1.0	400	87-95	0	500	Carrier gas not used.	29
26	"	(1.0)	100	64-76	600	500	Low reactant pressure. Melt sampled.	30
27	"	1.0	400	68-86	0	500	Repeat of Test 25.	31
28	"	1.0	100	82-94	0	500	Slow gas feed rate	32
29	"	1.0	800	88-100	0	500	Fast gas feed rate	33
30	"	1.0	800	82-83	0	500	Fast gas feed rate	34
31	"	1.0	800	77-95	0	500	Fast gas feed rate	35

TABLE 7
Summary of Data from Regeneration of
Synthetic Melts in the Bubble-Through Reactor

Regen. Test #	Melt Conditions			Melt Composition (wt %)		
	Temp. (°C)	Treatment Completed	Time (min.)	Melt Volume (ml)	M ₂ CO ₃	M ₂ S M ₂ SO ₄
22	430	NaOH+H ₂ S		150	80.4	25.1 -
	500	CO ₂	90	-	88.0	16.8 -
	500	CO ₂ + H ₂ O	30	-	96.5	4.6 -
	500	CO ₂ + H ₂ O	20	90	102.5	0.91 -
23	500	Regenerated melt		200	94.3	4.5 -
	500	Added 30g Na ₂ C		213	72.1	19.8 -
	500	CO ₂ + H ₂ O		200	95.0	1.4 -
24	500	make up		358	86.9	9.06 -
	500	CO ₂ + H ₂ O	71	358	93.4	1.54 -
25	500	make up	0	394	86.5	8.36 -
	500	CO ₂ + H ₂ O	71	394	91.7	0.82 -
26	500	make up	0	358	90.6	7.16 -
		CO ₂ + H ₂ O	127	358	94.8	2.20 5.7
		CO ₂ + H ₂ O	292	358	97.0	0.16 -
27	500	make up		430	90.0	8.23 -
	500	CO ₂ + H ₂ O	71	430	94.0	3.24 5.3
	500	CO ₂ + H ₂ O	261	430	95.0	0.0 -
28	500	make up		430	85.8	5.68 -
	500	CO ₂ + H ₂ O	82	430	94.2	3.17 -
	500	CO ₂ + H ₂ O	221	430	96.8	1.30 -
	500	CO ₂ + H ₂ O	411	422	91.6	0.25 -
29	500	make up		192	90.9	8.18 4.53
	500	CO ₂ + H ₂ O		192	100.9	1.84 4.31
	500	CO ₂ + H ₂ O		192	99.9	0.13 -

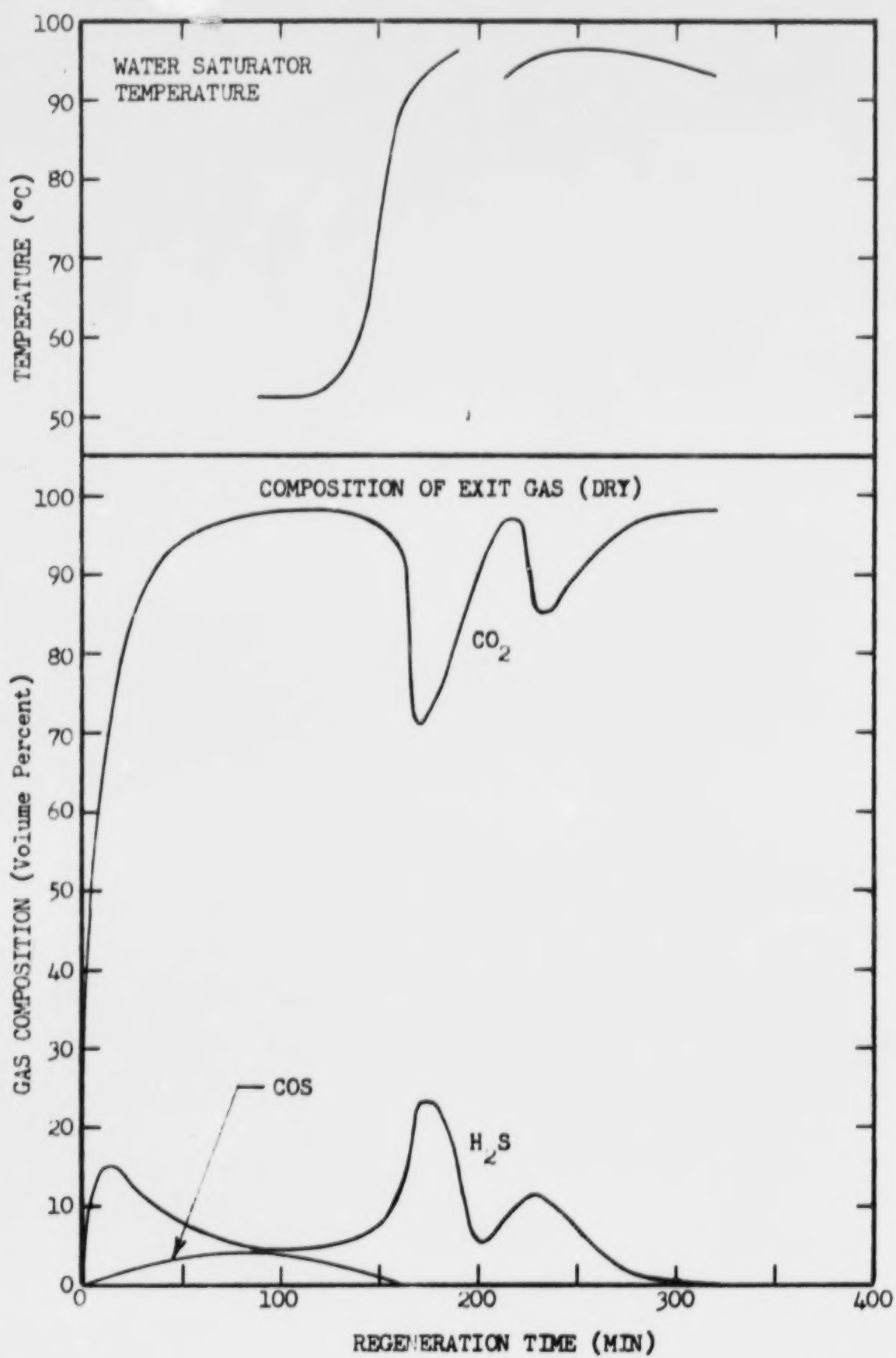


Figure 26. Regeneration of Melt Prepared by Neutralising NaOH with H₂S in Molten Carbonate (Test 22)

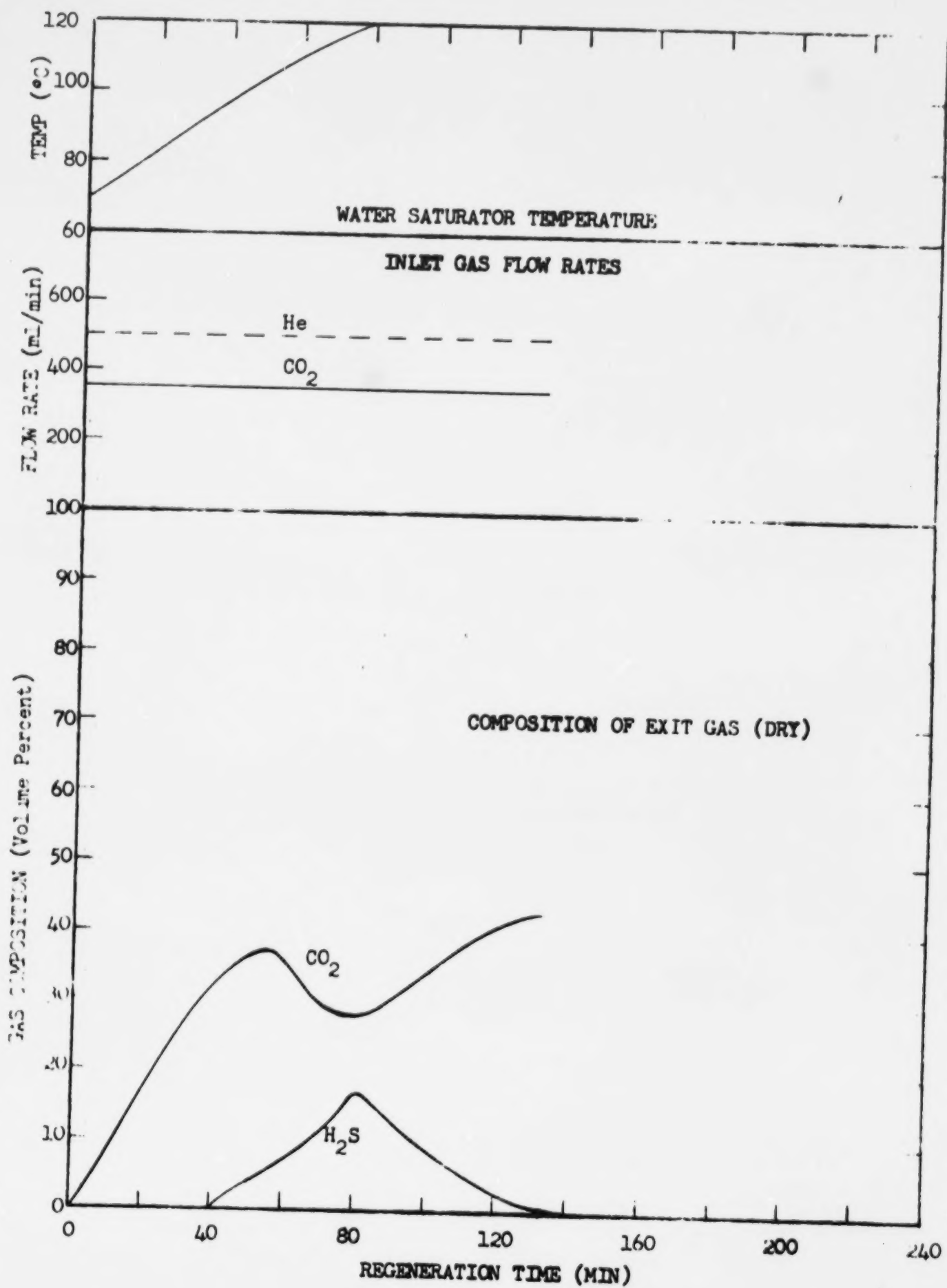


Figure 27. Regeneration of Synthetic Iron-Containing Melt at 3 Atm Pressure (Test 23)

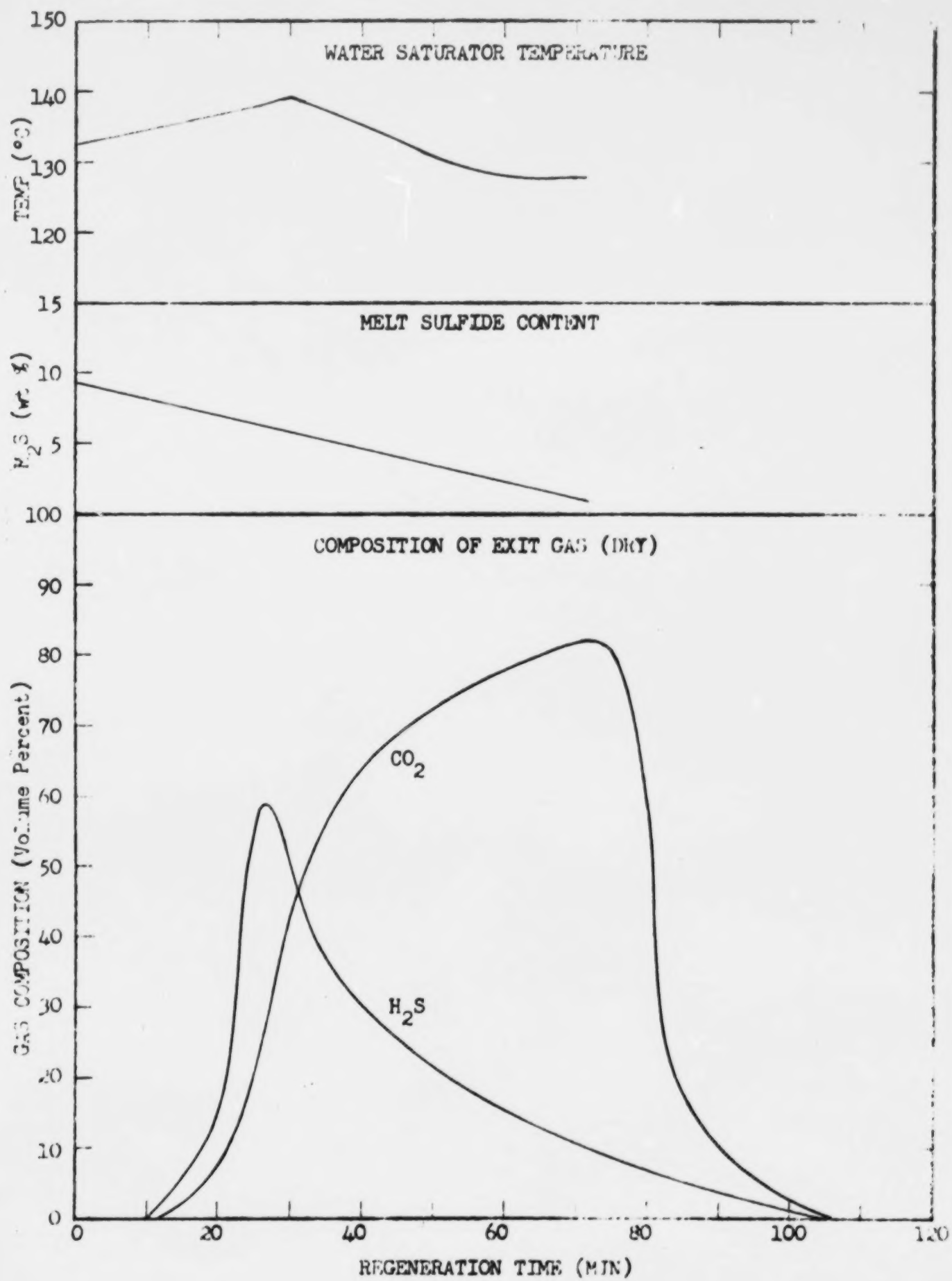


Figure 28. Regeneration of Synthetic Iron-Containing Melt at 4.9 Atm Pressure (Test 24)

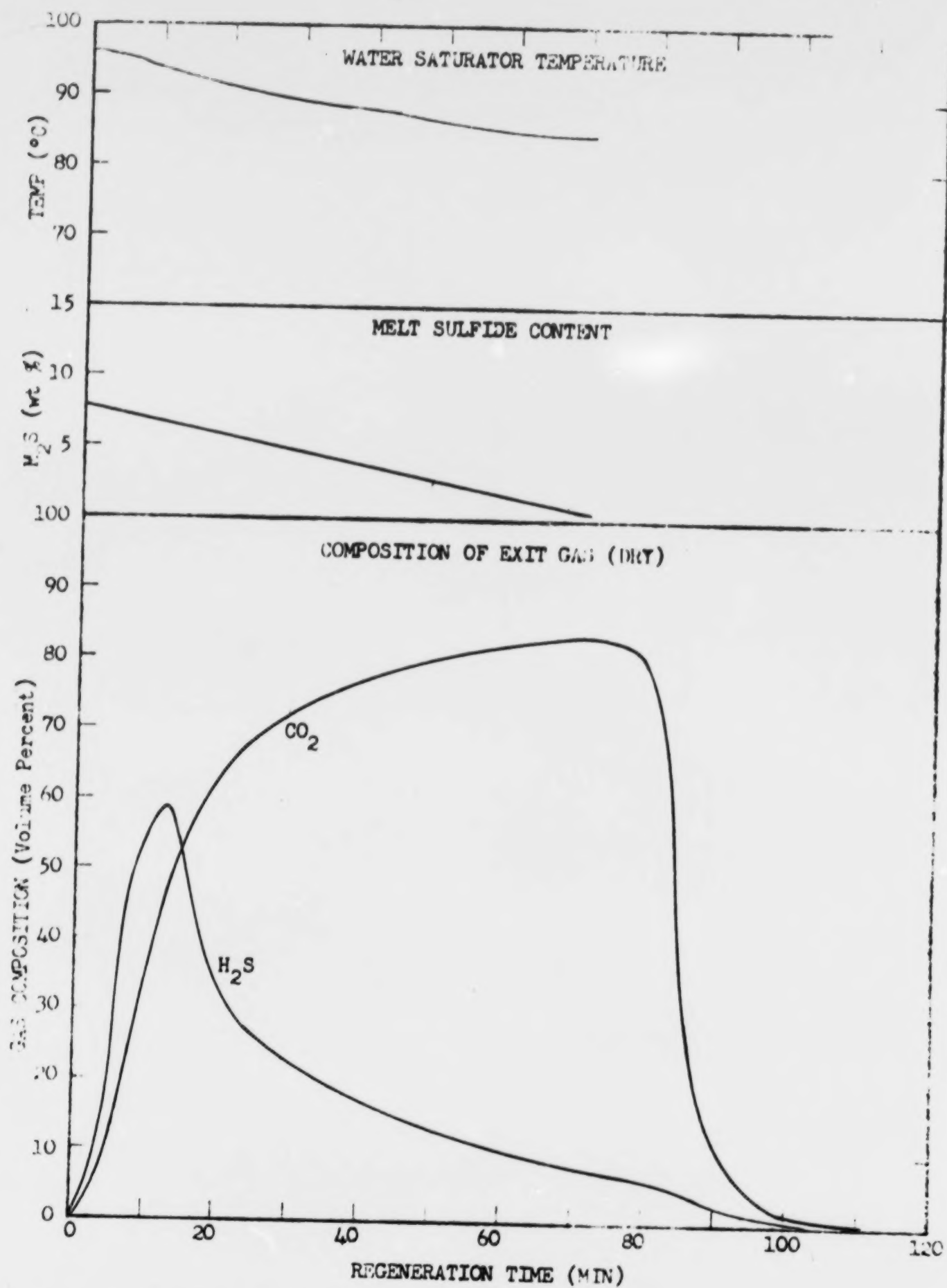


Figure 29. Regeneration of Synthetic Iron-Containing Melt at 1 Atm Pressure (Test 25)

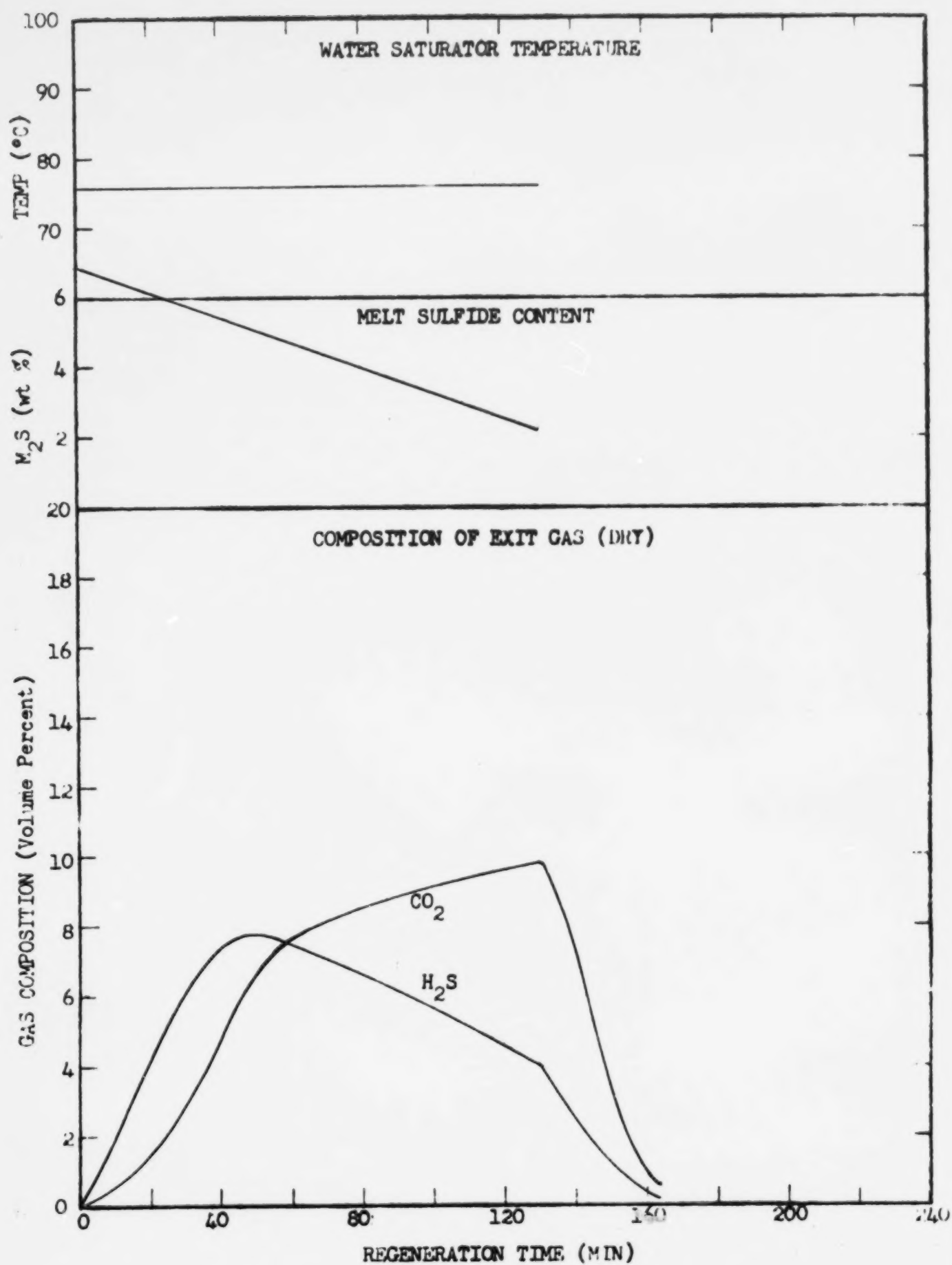


Figure 30a. Regeneration of Synthetic Iron-Containing Melt at 0.4 Atm Pressure, Part 1 (Test 26)

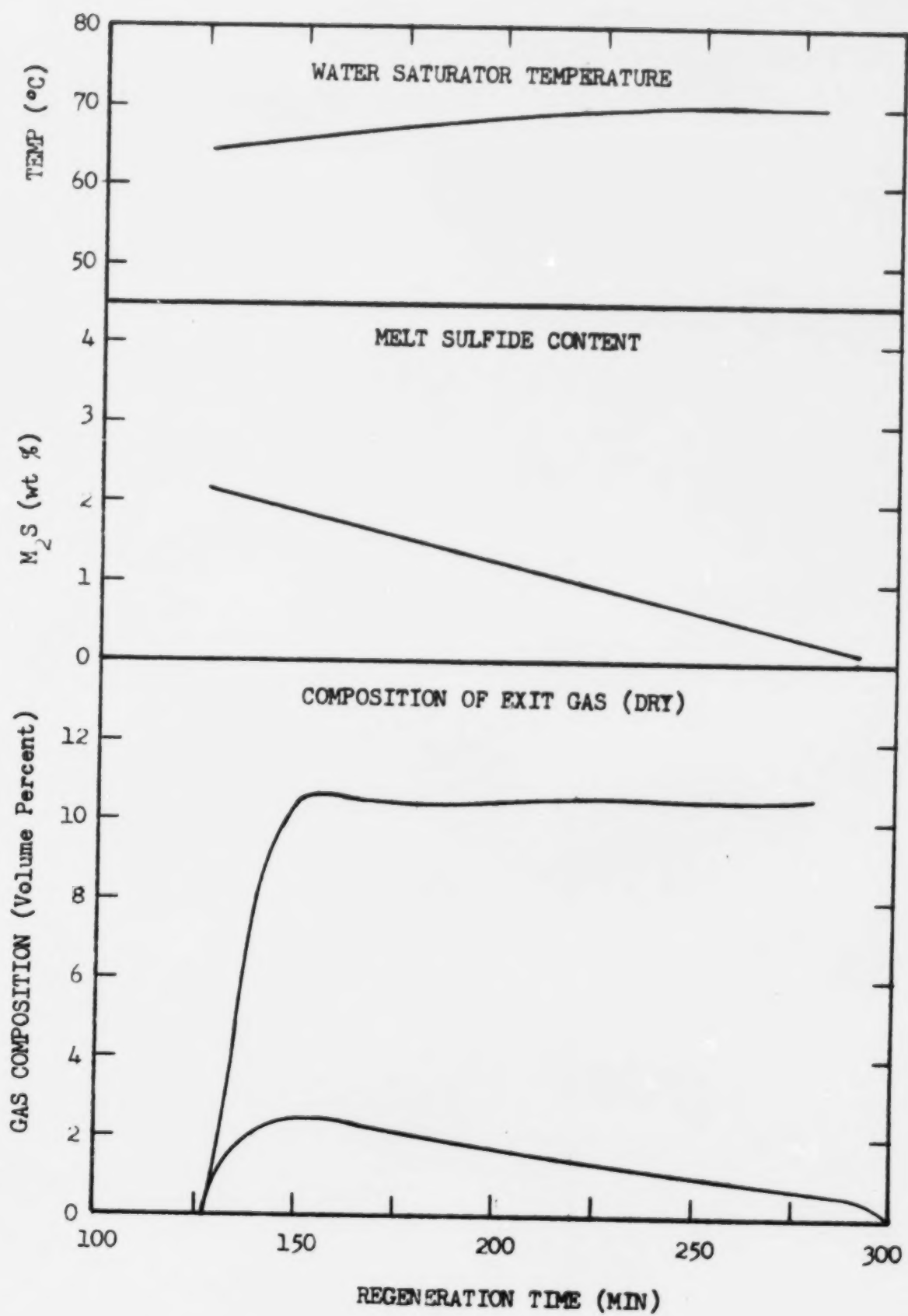


Figure 30b. Regeneration of Synthetic Iron-Containing Melt at 0.4 Atm Pressure, Part 2 (Test 26)

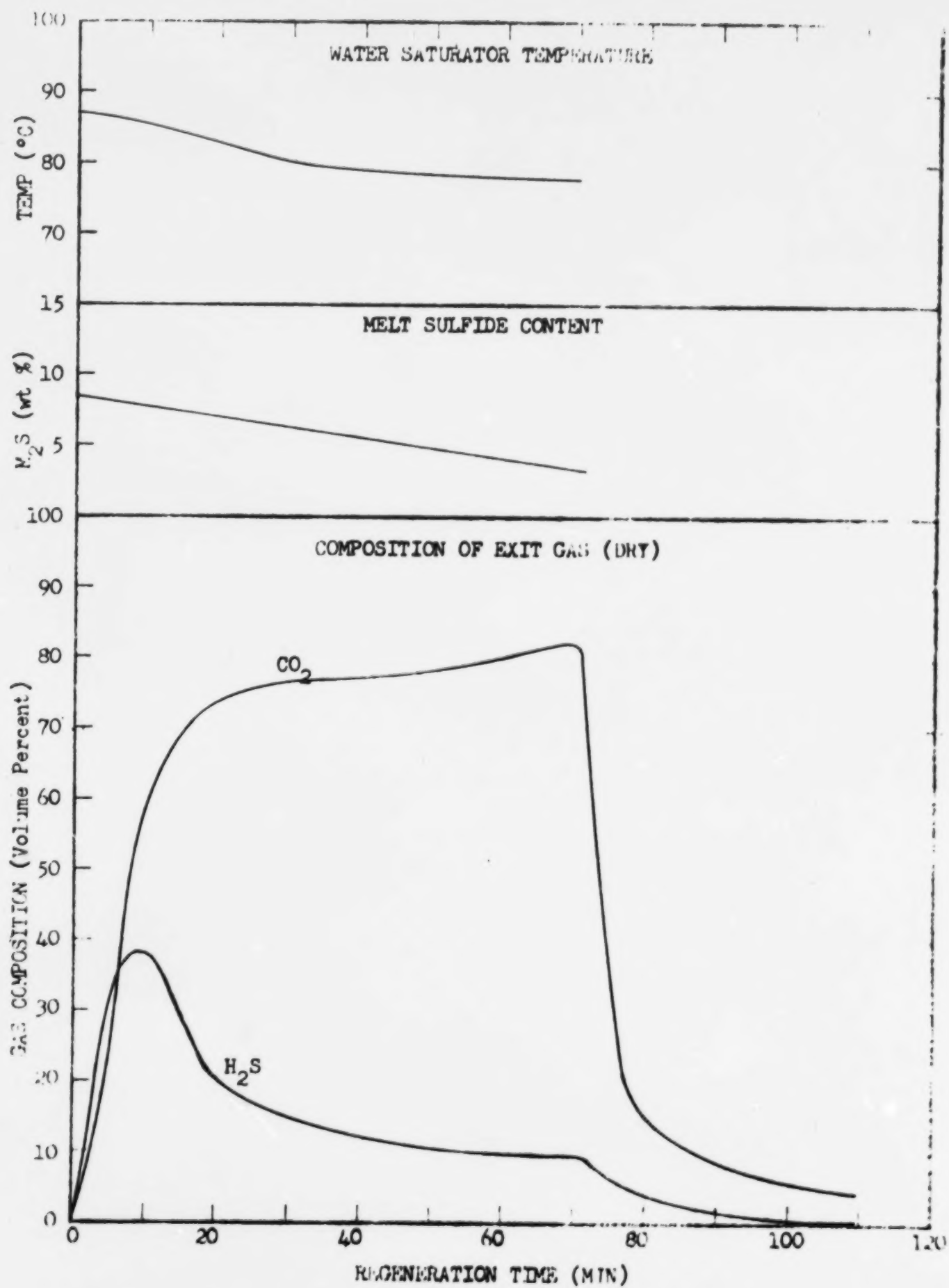


Figure 31a. Regeneration at 1 Atm Reactant Pressure, Part 1 (Test 27)

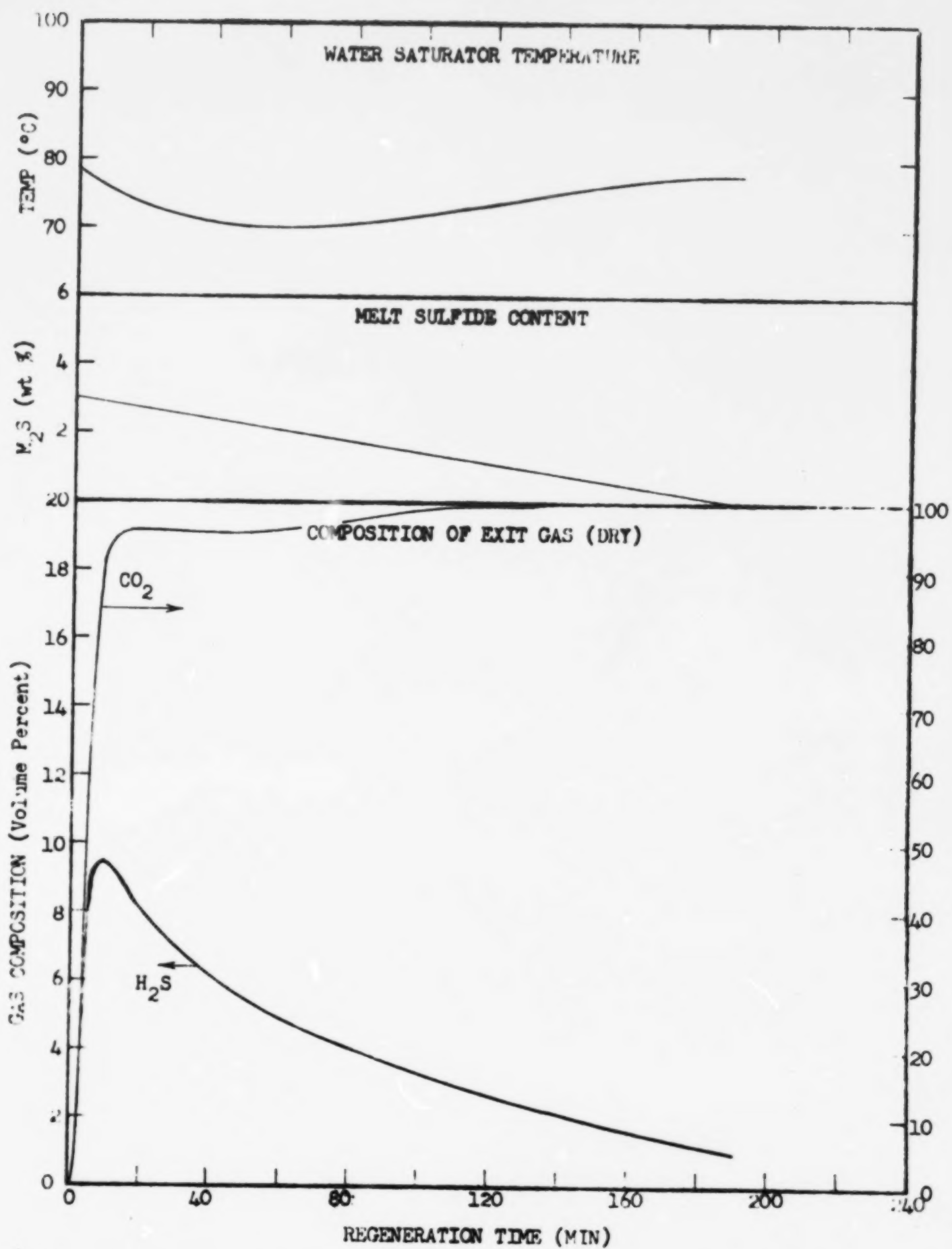


Figure 3lb. Regeneration at 1 Atm Reactant Pressure, Part 2 (Test 27)

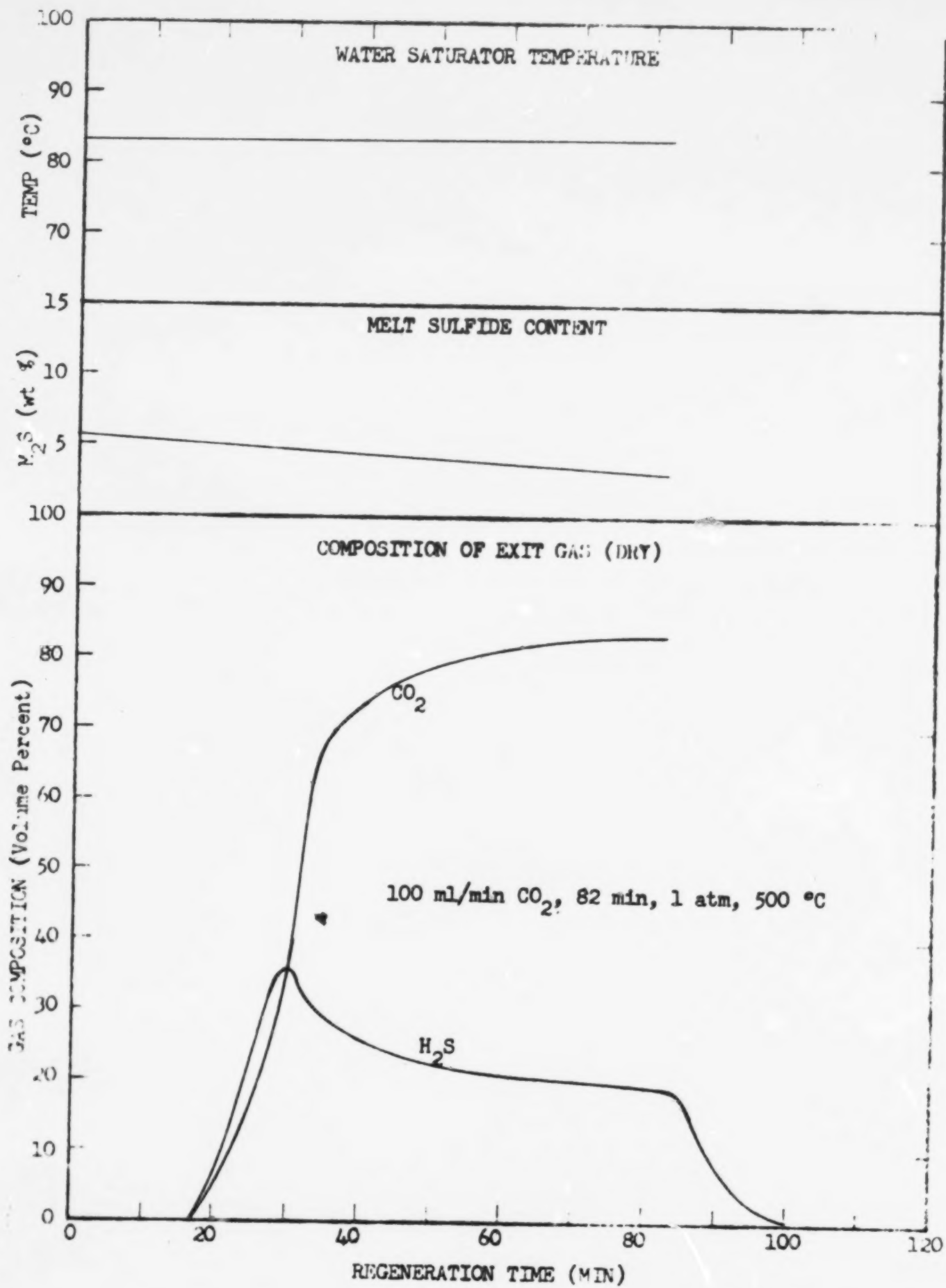


Figure 32a. Regeneration at Low Gas Flow Rate, Part 1 (Test 28)

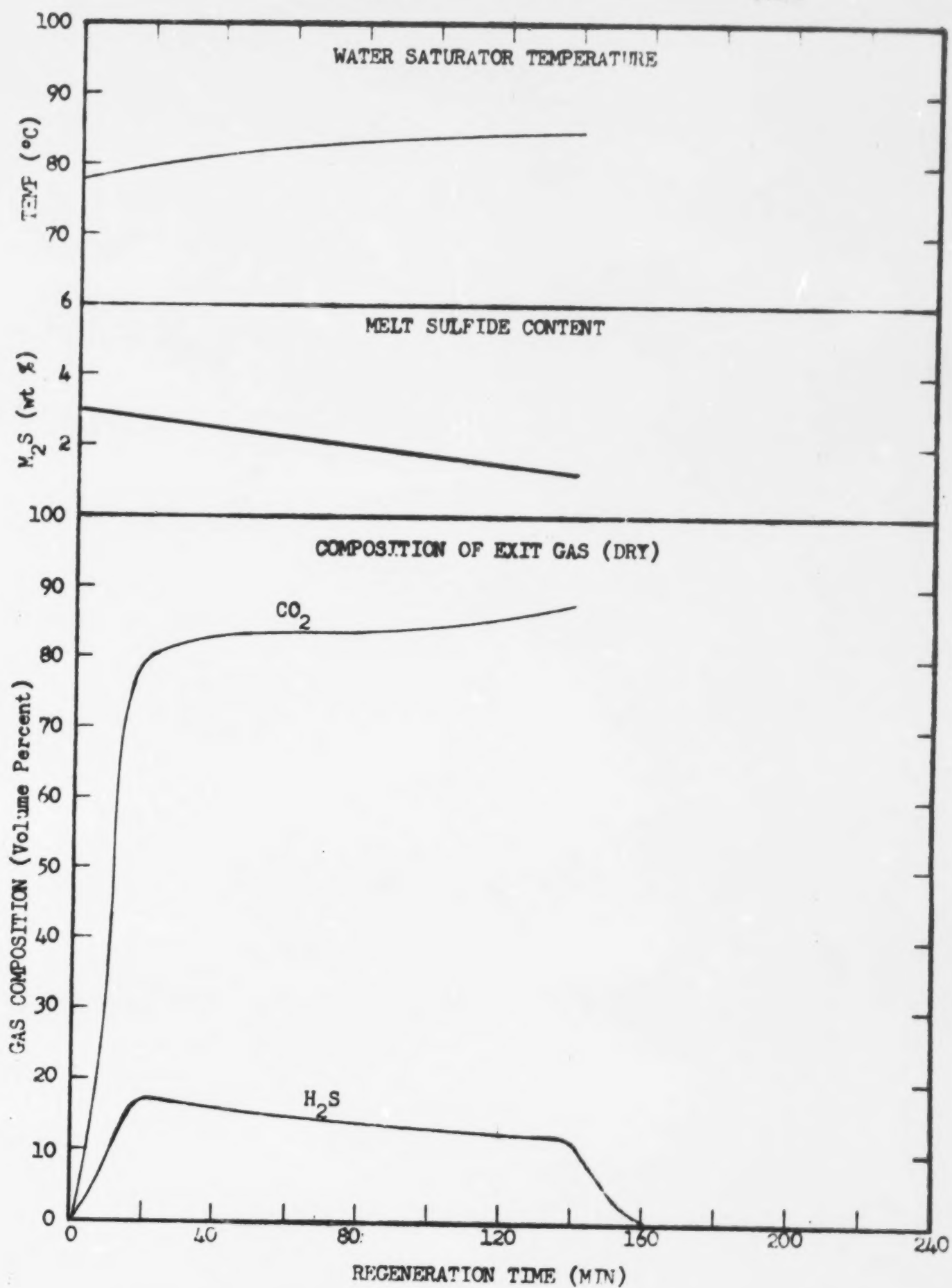


Figure 32b. Regeneration at Low Gas Flow Rate, Part 2 (Test 28)

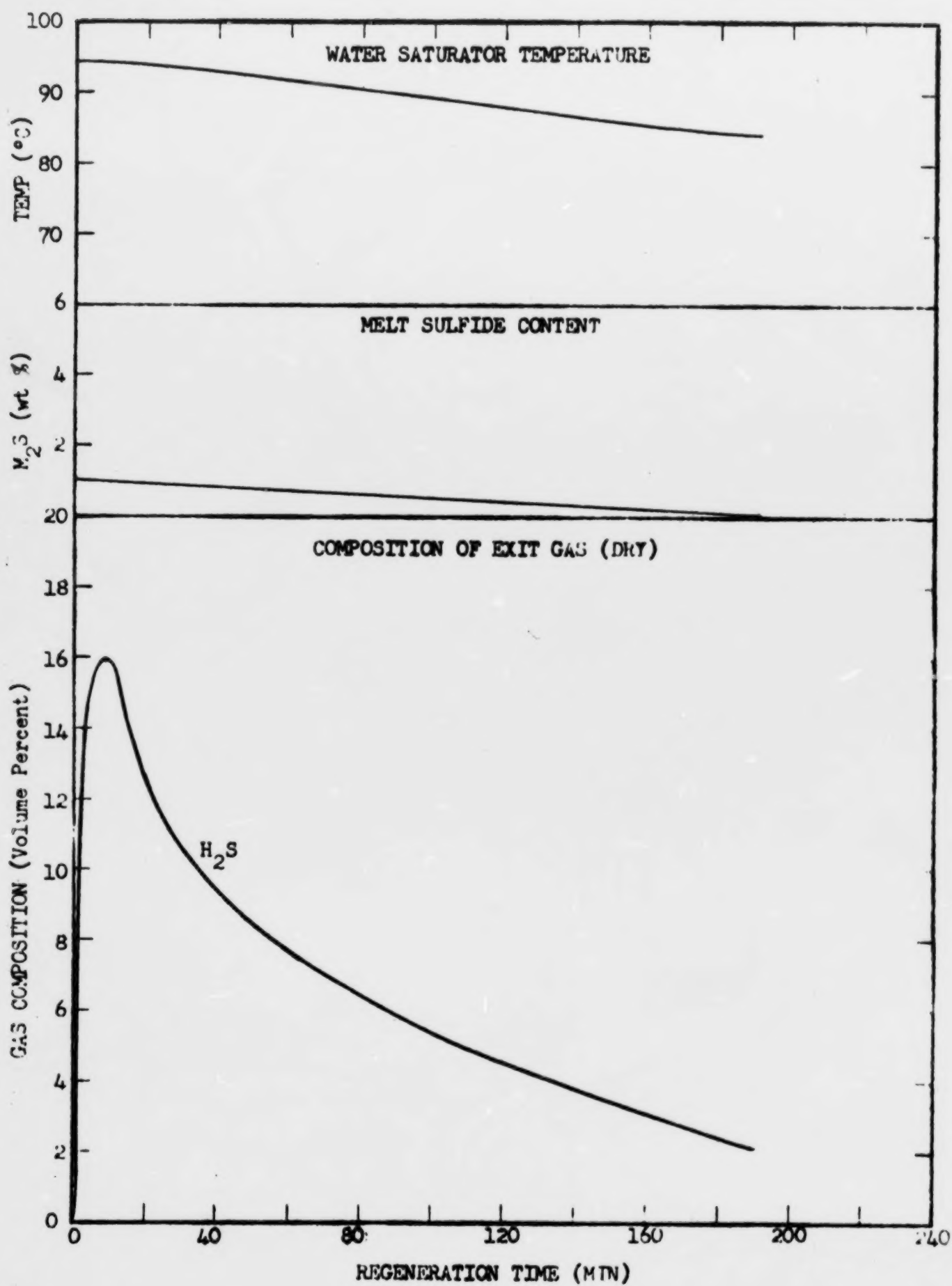


Figure 32c. Regeneration at Low Gas Flow Rate, Part 3 (Test 28)

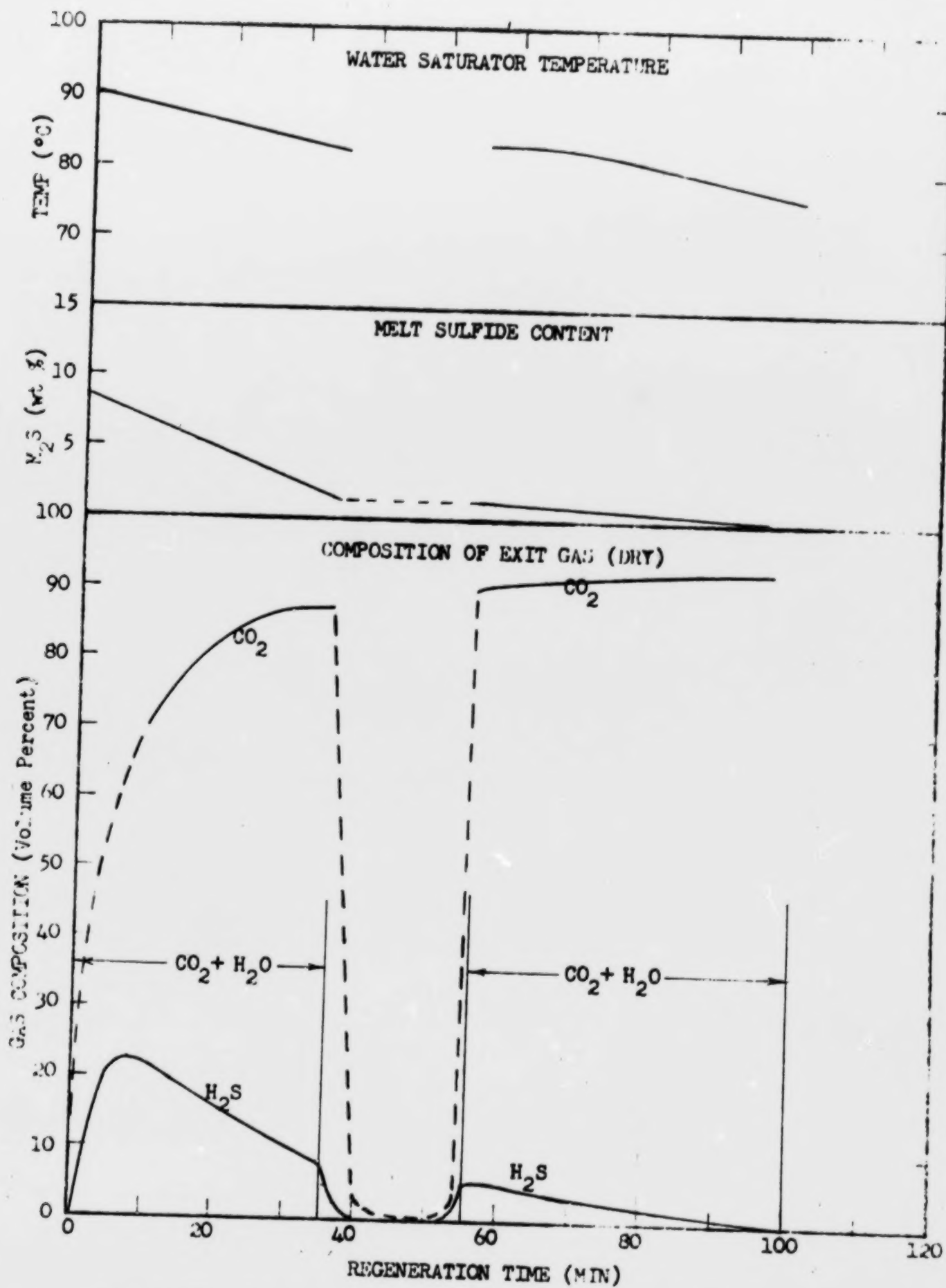


Figure 33. Regeneration at High Gas Flow Rate (Test 29)

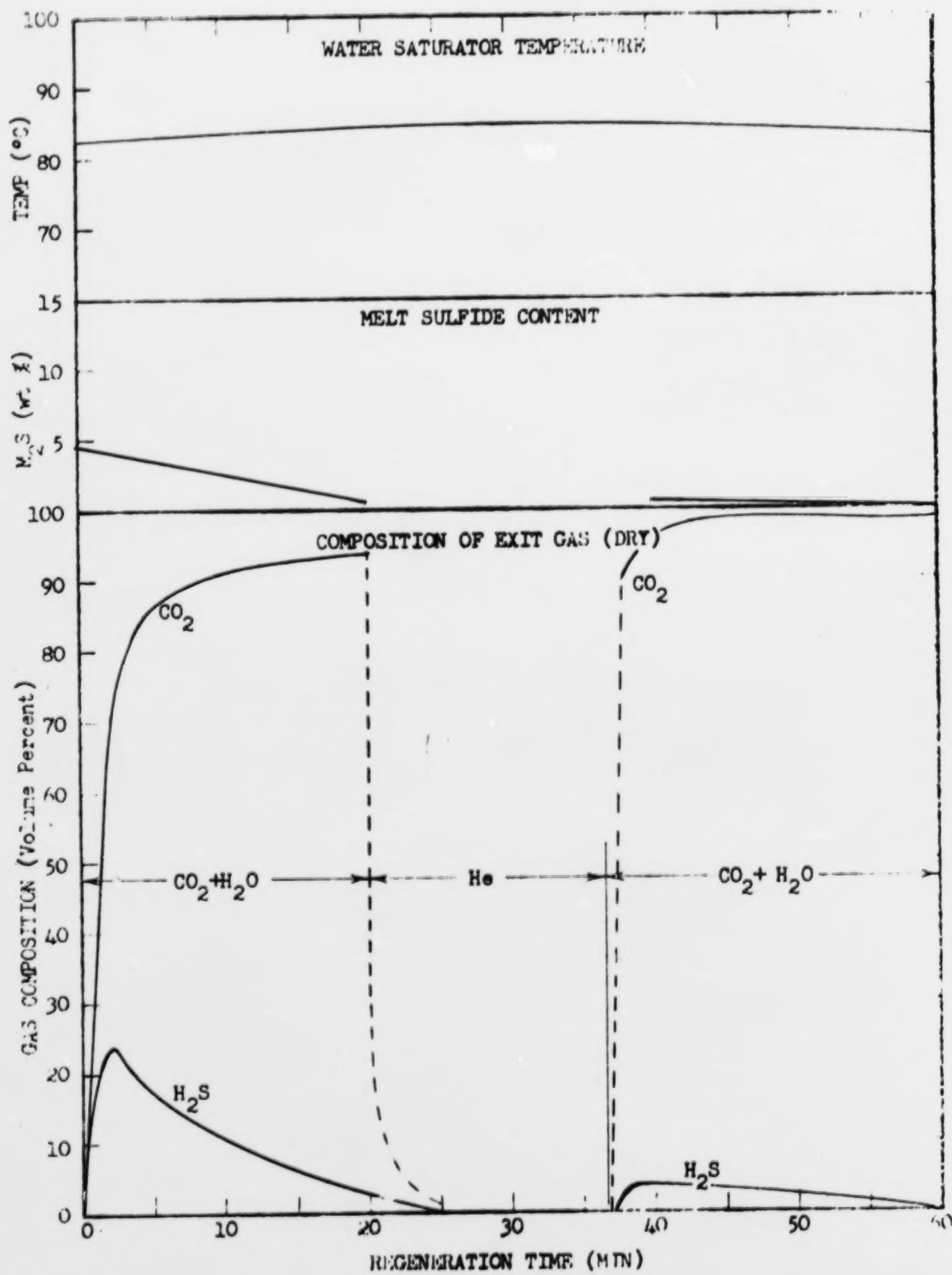


Figure 34. Regeneration at High Gas Flow Rate (Test 30)

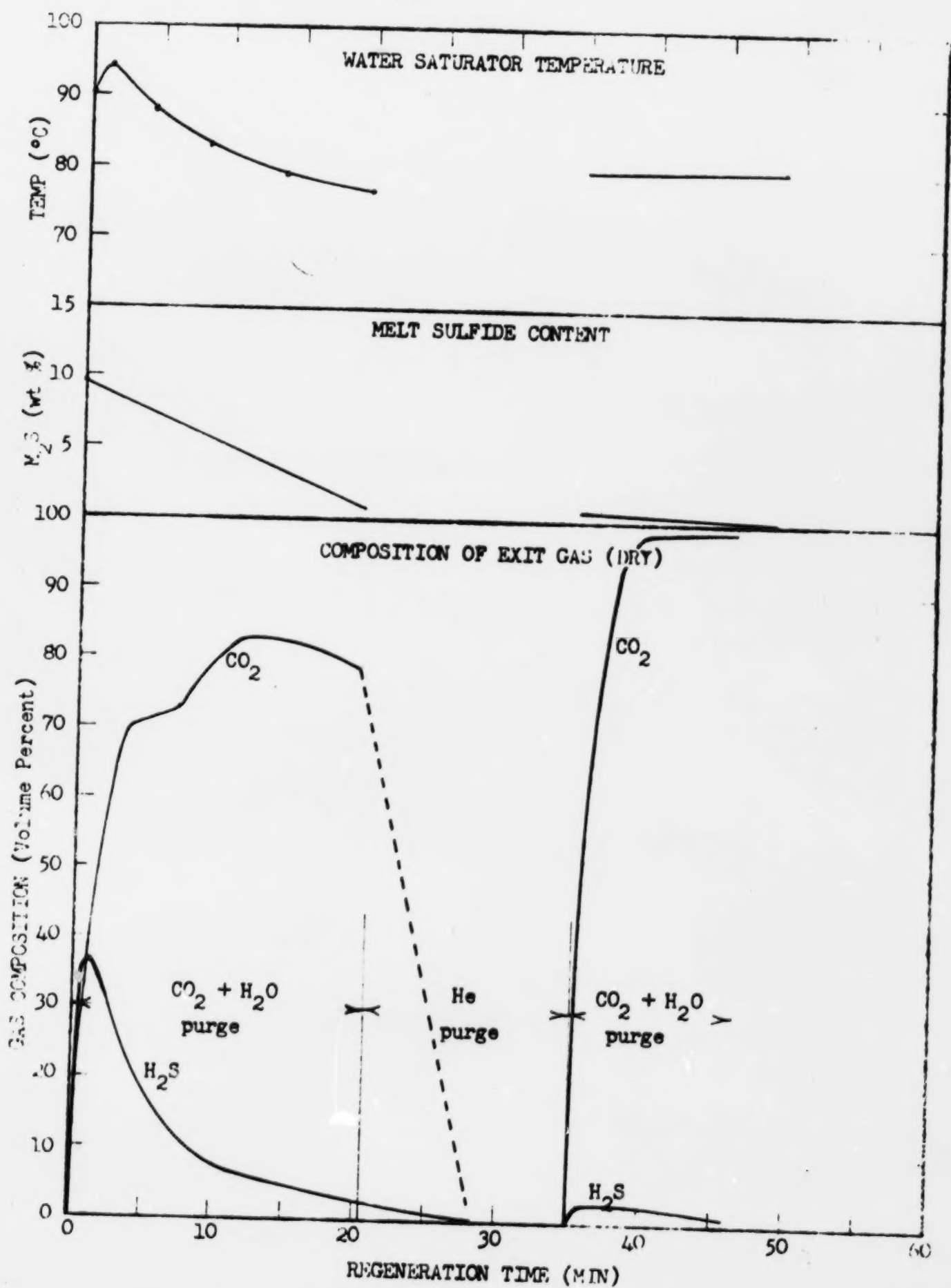


Figure 35. Regeneration at High Gas Flow Rate (Test 31)

amount of water evolved during this reaction was considerably less than the theoretical amount. Therefore, this melt was treated with dry carbon dioxide first to see if the water retained by the melt could be reacted and removed as hydrogen sulfide. Figure 26 shows that a substantial amount of hydrogen sulfide was evolved during the dry carbon dioxide treatment. Thus, water (or hydroxide ions) in some form was retained by the melt during the neutralization (reaction of hydrogen sulfide with hydroxide) used to prepare the melt.

During the regeneration carbon dioxide treatment, the hydrogen sulfide content of the exit gas gradually decreased to a low level, and the carbonyl sulfide content of the exit gas gradually increased to a 5 vol% level. The addition of water vapor to the feed gas caused the hydrogen sulfide content to increase to a high level and it then gradually decreased in a normal manner. The carbonyl sulfide decreased when water vapor was added to the feed gas. The final melt content after regeneration was 0.91 wt% sulfide. This amount was higher than expected (< 0.2 wt%) for a pure sulfide-carbonate melt. However, the melt appeared to contain a substantial amount of iron. Also, about one-third of the melt had been pushed out of the crucible into the containing envelope during the course of the regeneration, presumably due to foaming. The foaming was probably due to corrosion of the type 347 stainless steel crucible. This may have occurred in the process of preparing the sulfide melt by neutralization of sodium hydroxide with hydrogen sulfide. Graphite crucibles were used in the rest of the regeneration tests on synthetic melts.

The behavior during regeneration of the synthetic sulfide melt made by the neutralization of sodium hydroxide with hydrogen sulfide in molten carbonate was substantially different from that observed with reduced melts. Hydrogen sulfide could not be generated from reduced melts in appreciable

amounts by a dry carbon dioxide treatment; apparently reduced melts did not contain appreciable amounts of water or compounds that would yield water. Subsequent tests with synthetic melts made by adding anhydrous sodium sulfide to eutectic carbonate showed that these melts resembled those made from the reduction process. Therefore, the remaining tests with synthetic melts were made with sulfide melts prepared by adding sodium sulfide to eutectic carbonate melts.

5. The Effect of Pressure on the Regeneration Process

Regeneration tests 23 and 24 were carried out at pressures above one atmosphere (3 and 4.9 atmospheres, respectively). These higher pressure tests were carried out after a theoretical analysis (see part B, section IV) of the regeneration reaction based on an equilibrium reaction was completed. This analysis indicated that the amount of sulfide converted to hydrogen sulfide should be substantially higher (about double) with a pressure increase from 1 to 5 atmospheres.

Qualitatively, the results of regeneration tests at 3, 5 and 1 atmospheres (Figures 27, 28 and 29) did not indicate the expected substantial increase in conversion. Again, for an exact comparison, all of the variables, including melt sulfide content, water saturator temperature and inlet gas composition should be considered. When this was done as discussed in detail in section D, part IV, the analyses showed even less conversion at higher pressures. The data from regeneration test 26 (Figure 30) were obtained using a lower carbon dioxide inlet pressure. The analysis of the data from this test showed even higher conversion than was obtained at 1 and 5 atmospheres. These results, along with other evidence, led to detailed study and interpretation

of the carbon dioxide pressure effect on the regeneration process. This effect is discussed in detail in Section IV.

6. The Effect of Contact Time on the Regeneration Reaction

Regeneration tests 27-31 were carried out to determine if non-equilibrium conditions would be obtained by increasing the inlet gas feed rates to a high value. The regeneration data from these tests, shown in Figures 31 to 35, were compared with theoretical predictions based on equilibrium conditions. This comparison (part L, Section IV) indicated that equilibrium between the gas phase and the melt was being achieved even at the highest feed gas flow rate to melt volume ratio ($F/V = 1.28$ moles/minute per liter). These results show that the regeneration reaction is rapid, and that the regeneration step can be completed in a short time period of several minutes.

C. CYCLE TESTS IN THE BUBBLE-THROUGH REACTOR

1. Purpose

Six cycle tests were carried out during the course of this investigation. The purpose of the first three cycle tests was to test and demonstrate that the same melt could be used over again in the process cycle without losing its capacity to absorb sulfur dioxide. The purpose of additional cycle tests were to demonstrate (1) that sulfur could be recovered completely after the first cycle from melts containing iron and (2) that the iron recovered from regenerated melts could be used over again in the reduction step without loss in catalytic efficiency. The cycle tests were carried out as described in the experimental section.

Table 8 gives a list of the cycle tests that were carried out. Column 1 lists the cycle test number; columns 2 and 3 list the materials used for the crucibles and bubblers, respectively; column 4 lists the method used

TABLE 8

List of Cycle Tests with Bubble Through Reactor

Cycle Test No.	Crucible Material	Reactor Bubblers Material	Absorption Step (source of sulfur)	No. of Cycles Completed	Remarks
1	347 S.S.	304 S.S.	SO ₂ absorption	2/3	1st regeneration could not be completed because of extensive foaming.
2	347 S.S.	347 S.S.	SO ₂ "	2/3	1st regeneration could not be completed because of extensive foaming.
3	graphite	graphite	SO ₂ "	2 2/3	Emphasis on SO ₂ absorption step.
4	"	"	H ₂ SO ₄ addition	2	Iron catalyst disappeared.
5	"	"	H ₂ SO ₄ "	5	Main emphasis on sulfur recovery and catalyst recovery.
6	"	"	H ₂ SO ₄ "	4	Pressure above 1 atmosphere on the regeneration step.

to complete the absorption step; column 5 gives the number of cycles completed in the test, and column 6 lists remarks pertaining to the test.

2. Cycle Tests No. 1 and No. 2

In the first two cycle tests, steel bubbler-type contactors were used. In both cases, the absorption and reduction steps were successful but the melt foamed excessively when rapid regeneration was attempted, plugging the gas exit lines.

The absorption steps were carried out by bubbling pure sulfur dioxide into the melt at a rate of 165 ml/min. Quantitative absorption occurred, with no sulfur dioxide detectable in the carbon dioxide stream given off. The reduction steps were then done with hydrogen at 1110°F (600°C). In both cases, 5 hours were required to achieve complete reduction. This was relatively rapid (about twice as fast as expected) considering the fact that a bubbler contactor was used, and reflected the catalytic activity of iron corrosion products. The first regeneration was then tried with a water-saturated carbon dioxide flow rate of 2.5 l/min., and resulted in copious foaming which plugged the exit gas line as the salt carried in the foam solidified. The regeneration for the second cycle test was attempted at a slower inlet gas flow rate (0.9 l/min.); foaming again caused the exit lines to plug. The foamed salt was brown colored, indicating that substantial amounts of corrosion products were present. These impurities may have caused the melts to foam excessively. In the remaining cycle tests, graphite crucibles and bubblers were used to reduce the amount of added impurities. In addition, low gas flow rates were used to decrease the possibility of excessive foaming.

3. Cycle Test No. 3

The third cycle test was performed using a graphite bubbler and crucible (to eliminate iron) and slow regeneration rate (150-300 ml/min.), to study the effect of cycling on the carbonate melt. Two and two-thirds cycles were completed, with the results summarized in Table 9.

The three absorption steps were all quantitative, with no sulfur dioxide detectable in the off-gas. It should be noted that the second and third absorptions were done with melts containing 19% and 10% sulfate, respectively, with no detectable loss in capacity for sulfur dioxide, or in absorption rate. This is significant, because it shows that the process can be operated successfully with incompletely-regenerated melts.

The first regeneration step was quite successful, and yielded essentially pure carbonate. The time required was probably determined by the low reactant feed rate (150-300 ml/min. of water-saturated carbon dioxide) rather than by the rate of reaction. Sulfur recovery was also good, 90% being recovered as hydrogen sulfide and the remainder probably also evolved but lost during sampling.

The first reduction step was very slow, due to the combination of (1) no iron catalyst present, and (2) relatively low temperature (1050°F). The reduction was so slow that it was terminated after ~ 11½ hours, although only 36% of the sulfate and sulfite was reduced. The incompletely-reduced melt was then completely regenerated to carbonate plus sulfate, with only 0.2 wt% sulfide remaining. This time, however, only 70% of the sulfur was recovered as hydrogen sulfide. It is thought that this relatively low recovery was due, in part at least, to a portion of the melt freezing out above the bulk of the melt because of the lower temperature during regeneration (860°F,

TABLE 9

Summary of Results from Cycle Test No. 3

Step	Time (min)	Temp (°F)	Gas and Flow Rate (ml/min)	Melt Composition (wt %)				Comments
				M ₂ CO ₃	M ₂ SO ₃	M ₂ SO ₄	H ₂ S	
Start	0	905	He, 200	91.0	0	-	11.1	Melt as prepared
Regeneration	180	905	CO ₂ +H ₂ O, 150-300	99.4	0	-	0.2	90% H ₂ S Recovery
Absorption	60	905	SO ₂ , 165	64.5	27.2	3.7	0.2	Complete absorption
Reduction	247	1050	H ₂ , 1100	68.2	0	21.2	10.2	29% reduced
	683	1050	H ₂ , 1100	67.5	0	19.3	11.7	36% reduced
Regeneration	208	860	CO ₂ +H ₂ O, 150	81	0	19.1	0.2	70% H ₂ S Recovery
Absorption	50	896	SO ₂ , 165	58.5	17.2	21.1	0.4	Complete absorption
Reduction	185	1290	H ₂ , 1100	61.9	0	8.1	28.6	Note 1
Regeneration	217	880	CO ₂ +H ₂ O, 150	84.9	0	9.6	0.3	90% H ₂ S recovery
Absorption	40	880	SO ₂ , 165	45.7	7.5	39.8	3.4	Complete absorption

Note 1. An excess of sulfide (~ 10 wt%) was found at the end of this reduction step. It may have come from sulfide-rich foam formed during the previous regeneration step, which solidified above the melt until the temperature was raised for the reduction step. This would also account for the low sulfur recovery of the previous regeneration step.

460°C). Further evidence for this was obtained at the end of the second reduction step, when about 10 wt% too much sulfide was found in the melt. Apparently the solid portion remelted at the higher reduction temperature, and recombined with the rest of the melt.

The second reduction was done at 1290°F, at which temperature about 60% of the sulfate was reduced in 3 hours.

The third regeneration was also essentially complete, with good sulfur recovery.

This cycle test demonstrated that regenerated carbonate does not lose its capacity for absorbing sulfur dioxide, even when a large amount of sulfate is recirculated. However, it was not an accurate demonstration of the reference process cycle, because the reference cycle requires that the reduction and regeneration be done in two different large-surface-area contactors, instead of a single bubbler contactor. Also, a catalyst would probably be required in the reduction step, and the melt properties may be different to some extent depending upon whether the catalyst is circulated through the entire process or removed ahead of the absorber.

4. Cycle Test No. 4

Cycle Test No. 4 was carried out involving two reductions and two regenerations in the order, Reduction-regeneration - reduction-regeneration. This test was carried out with a melt containing 2.4 wt% iron at the start, to determine (1) the effectiveness of the iron as a reducing catalyst in the second reduction cycle, and (2) if all of the sulfur added to the melt after the first regeneration could be recovered completely in succeeding regeneration steps.

Equal weights (25g) of lithium, sodium and potassium sulfate were added to a regenerated melt which contained iron. This melt, with added alkali metal sulfates, was reduced in the usual manner with hydrogen and then regenerated in the usual manner with carbon dioxide and steam. Table 10 shows the melt compositions, including the iron concentration before and after the treatments, the amount of sulfur recovered from each regeneration, and other data collected during the test. During the regeneration of melts containing iron, most of the iron and a substantial amount of sulfide (15-25%) was usually deposited on the crucible wall above the melt line. When the melt temperature was raised from the regeneration temperature ($\sim 500^{\circ}\text{C}$) to 600°C for the reduction, this deposit either became more fluid and flowed down into the bulk of the melt or it was eroded away by melt splashing up during the reduction step and ended up in the melt. The latter appeared to be the case, as indicated by the manner in which the iron concentration (Table 10) increased during the course of the second reduction step in cycle test 4. However, this test was discontinued after the second cycle because the melt iron content appeared to remain low (in fact it decreased) after the regenerated melt had been heated at 600°C for 6 hours with a helium purge. The reduction step would require too long a time period without iron in the melt. It appeared that sulfate in the melt or a hydrogen purge was needed to remove the iron-containing deposit from the walls in tests of this type. Sulfate may form a suitable flux, or hydrogen may reduce some component to make a lower melting mixture.

The reactor was cooled after the second cycle had been completed and the froth (deposit from the walls of crucible) from the regeneration was mixed with the residue melt, remelted to 450°C in a pressure filtering device and filtered. The filtrate from this test was a clear melt which solidified

TABLE 10

Summary of Results from Cycle Test No. 4

Treatment or Melt ^a	Reactants and Conditions				Melt Composition (wt %)				Percent Sulfur Recovered as H ₂ S	
	Reactants	Time ^b (hr)	Temp. (°C)	Height (in.)	M ₂ CO ₃	M ₂ SO ₄	H ₂ S	Fe	Based on Sulfate Added	Based on H ₂ S Melt Conc.
Make-up salts melted	He purge	0	600	3.2	67.8	25.1	0	2.4		
First reduction	H ₂	(10)	600	2.8	78.5	-	19.8	2.4		
First regeneration	CO ₂ , H ₂ O	3.5	500	2.6	100.0	-	1.53	0.32	55	54
Added 75g M ₂ SO ₄ to Regenerated Melt	He purge	1.0	600	3.2	72.4		0.32	0.43		
Second Reduction	H ₂	4.0	600	3.2	72.5	17.69	9.36	1.06		
Second Reduction	H ₂	8.0	600	3.2	76.4	2.38	20.7	1.40		
Second Regeneration	CO ₂ , H ₂ O	4.3	500	2.6	99.4	3.14	1.10	0.24	81	66
Regenerated Melt ^c 72 hr @ 500°, 6 hr @ 600°	He purge	78	500- 600	2.0	94.4	-	0.21	0.08		

^a Salts used in make-up of melt: 100g Li₂CO₃, 100g K₂CO₃, 52.4g Na₂CO₃, 64.3g Na₂SO₄, 40.3g FeSO₄ 7H₂O.

^b Time after treatment started.

^c The froth deposit after the second regeneration contained 58.0% M₂CO₃, 24.8% H₂S and 6.0 wt% iron.

to a white solid containing less than 0.1 wt% sulfide and 25 ppm iron. The residue remaining on the porous sintered metal filter was a black material containing 8.0 wt% sulfide and 6.56 wt% iron. This clearly showed that the sulfide which was not regenerated was in a form which was not appreciably soluble in the melt, and that the bulk of the iron was insoluble in the melt at this temperature.

5. Cycle Test No. 5

Cycle Test No. 5 was carried out involving five reductions and five regenerations in the order, Reduction-regeneration-add alkali metal sulfates-reduction-regeneration, etc. This test was performed with a melt containing 2.4 wt% iron at the start. After each reduction step, the melt was regenerated in the usual manner with carbon dioxide and water vapor and then equal weights (25g) of lithium, sodium and potassium sulfates were added to the regenerated melt. Table 11 shows the melt compositions, including the iron concentration after each step in the cycle; the amount of sulfur recovered from each regeneration; and other data collected during the test. The steps in each cycle are given in column 2. The reduction steps were carried out using hydrogen at 600°C except in cycles 1 (hydrogen and steam at 650°C) and 3 (hydrogen at 650°C). The sulfide concentration after each regeneration decreased from 3.9 to 0.6 wt% sulfide (column 7). This gradual decrease from cycle to cycle probably was caused by a gradual loss of iron from the melt (column 9). Also, a greater fraction of the iron that did remain was being removed with the froth during the latter regeneration steps. The reason for this was not known. During the reduction step for cycle No. 4, the iron content (column 9) increased gradually during the reduction step. Although data (salt sample analyses at stages of the reduction step) were not obtained for the reduction

TABLE 11
Summary of Results from Cycle Test No. 5

Cycle No.	Cycle Step	Melt Conditions			Melt Composition (wt %)			
		Temp (°C)	Height (in.)	Color	M ₂ CO ₃	M ₂ S	M ₂ SO ₄	Fe
1	Make-up Salt Melted	600	3.5	Dark	72.7	0.5	26.4	(2.4)
	Reduction 1	600	3	Black	71.9	18.9	0.7	1.74
	Cooled	500	4.2	Black	78.5	13.6	-	2.16
	Regeneration 1	500	3.5	Grey	95.5	3.86	-	1.77
	Add 75g M ₂ SO ₄	500	-	-	-	-	-	-
	Heated to 600°C	600	4.5	Brown	74.5	4.7	18.7	1.66
2	Reduction 2	600	4.5	Black	80.0	13.0	0	-
	Cooled to 500°C	500	4.5	Black	75.7	14.2	0.7	1.97
	Regeneration 2	490	3.6	Grey + ppt	100	2.1	0.6	0.63
3	Added 75g M ₂ SO ₄	600	-	-	-	-	-	-
	Reduction 3	650	4.7	Black	81.6	21.8	0	1.66
	Cooled to 500°C	500	4.7	Black	80.2	19.8	0	1.55
	Regeneration 3	503	4.3	Grey + ppt	95.4	1.7	0	0.78
4	Added 75g M ₂ SO ₄	600	5.2	Dark	73.7	3.0	10.2	1.05
	Reduced 2.8 hr	592	5.2	Black	80.3	3.6	16.7	1.10
	Reduced 7.1 hr	600	4.7	Black	78.6	8.8	7.3	1.03
	Reduced 10.2 hr	600	4.6	Black	80.4	13.6	4.4	1.21
	Reduced 13.3 hr	600	4.5	Black	84.0	14.8	0	1.69
	Regenerated 3.5 hr	500	4.0	Grey	93.0	1.8	-	0.17
	Regenerated 6.8 hr	500	3.6	Grey	100.9	0.6	-	0.29
	Removed 50g of Salt	Filtrate		White	96.4	0	0	3 1/4 ppm
5	Added 75g M ₂ SO ₄	600	4.1	Brown	75.2	0.81	23.1	-
	Reduction 5	600	4.0	Black	85.5	21.7	-	1.45
	Regeneration 5	480	3.8	Grey	97.7	0.06	-	0.01
	Froth after 5th Regeneration			Black	69.9	18.5	0.12	5-14

step in the other cycles, the behavior observed in the cycle 4 reduction step is probably typical. The additional regeneration data for each cycle are shown plotted in Figures 36-40. A comparison of the curves reveals that the melts behaved about the same during each regeneration.

Table 12 shows the summary of the reduction and regeneration times for each cycle and also the percent of the added sulfur recovered as hydrogen sulfide from each regeneration. The most important result of the cycle test, the sulfur recovery values, are shown in column 4. The high (91-114%) sulfur recovery values obtained show that the sulfur can be recovered completely as hydrogen sulfide after the first cycle. The first cycle gave a low recovery value because iron tied up a sizeable fraction of the sulfide in a nonregenerable form; but after the first cycle, any sulfur added to the melt (as sulfate) could be recovered during regeneration. This shows that there are no important side reactions yielding sulfur compounds in some form other than hydrogen sulfide.

Table 13 gives a summary of the materials (reactants) added and removed in cycle test No. 5. The data in this Table represents the raw analytical data from which the sulfur recovery values given in Table 12 were calculated.

6. Cycle Test No. 6

In Cycle Test No. 6, four pressure regenerations were completed. Three of these were with sulfide melts made by reducing sulfate-bearing melts with hydrogen, using iron as the catalyst. One regeneration was made with a synthetic sulfide melt. After the first and third regenerations, equal weights of lithium, sodium and potassium sulfate were added to the regenerated melt in preparation for the next reduction step. The sulfate was then reduced with

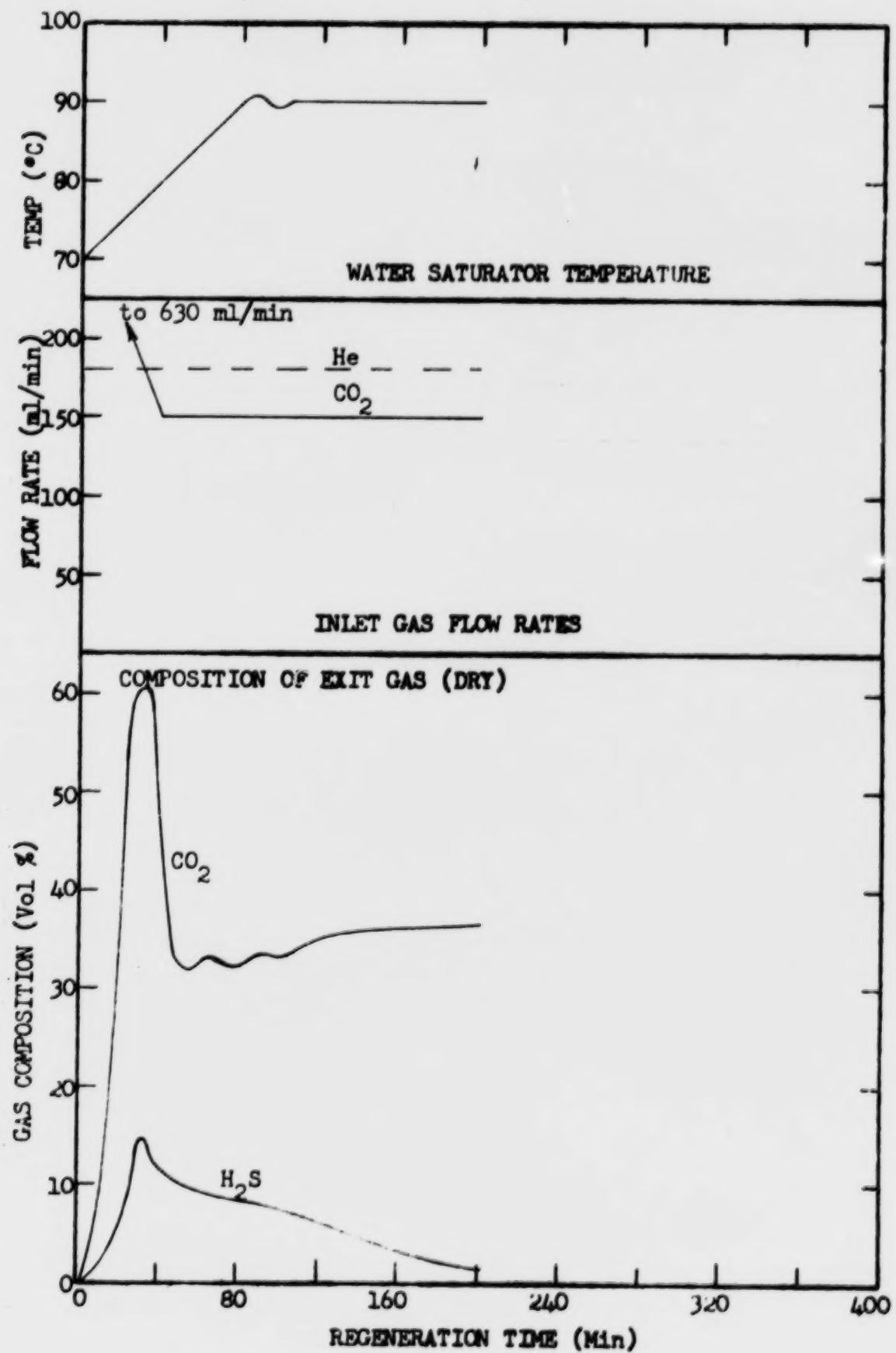


Figure 36. First Regeneration, Cycle Test 5

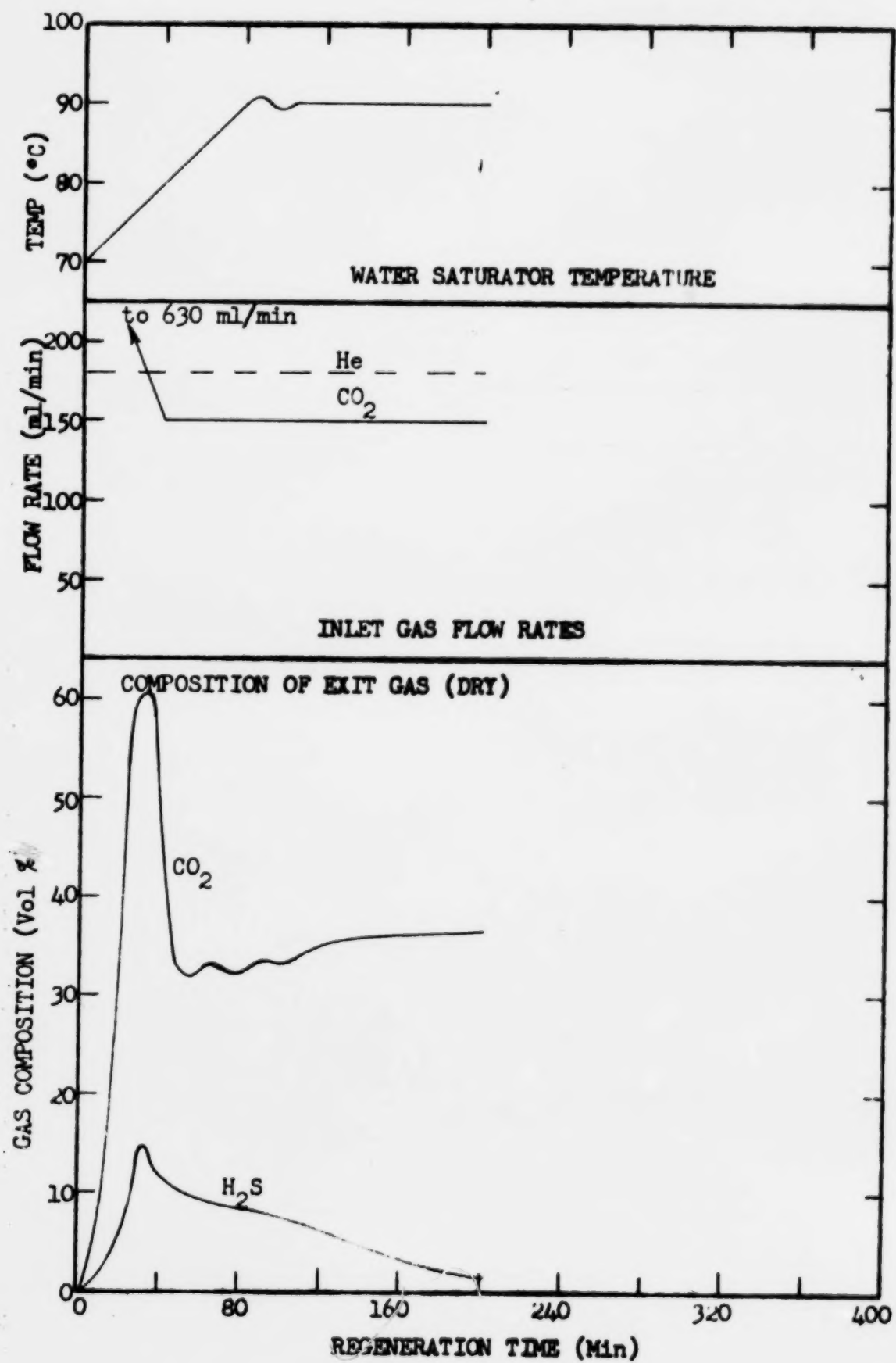


Figure 36. First Regeneration, Cycle Test 5

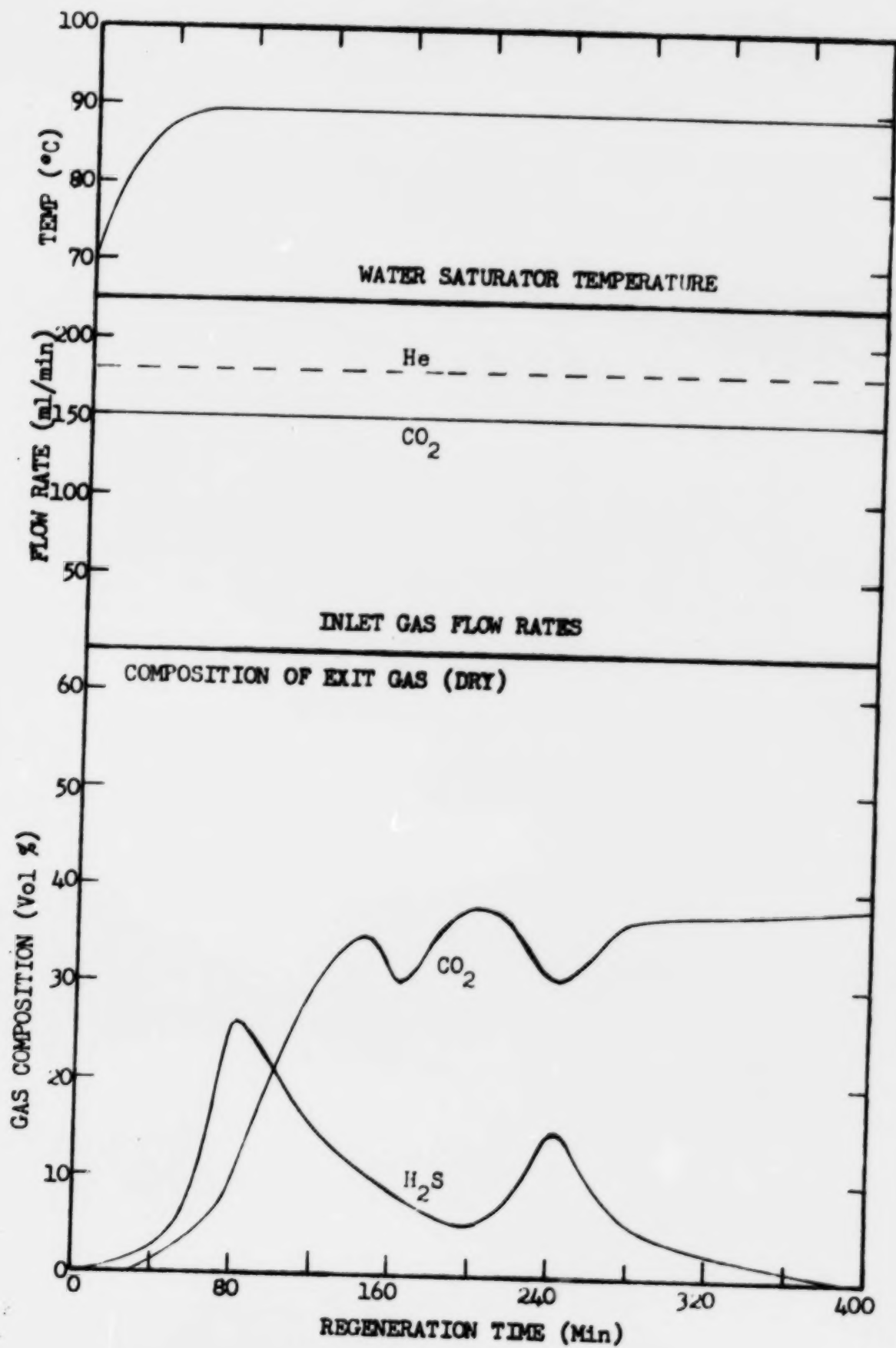


Figure 37. Second Regeneration, Cycle Test 5

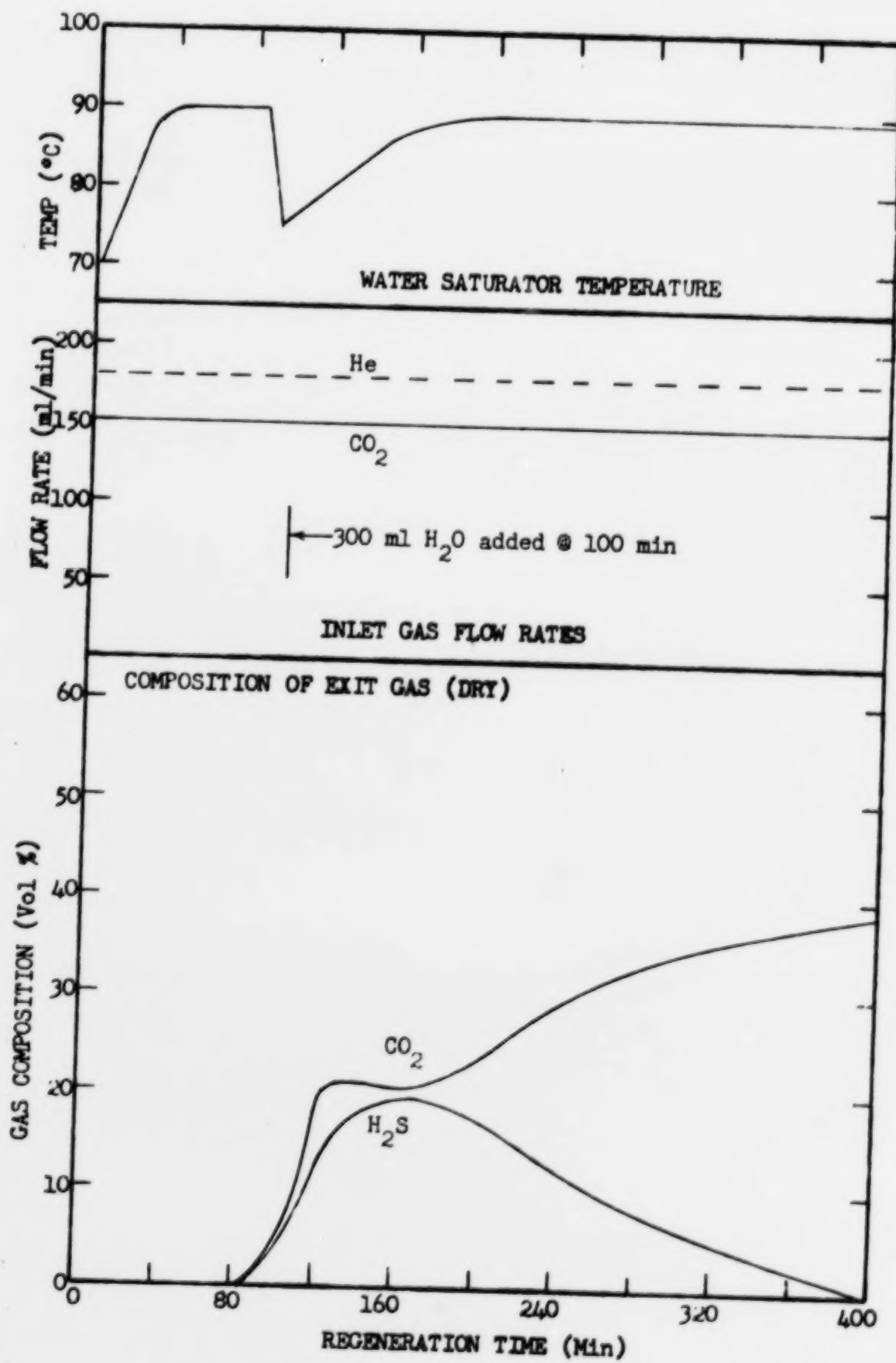


Figure 38. Third Regeneration, Cycle Test 5

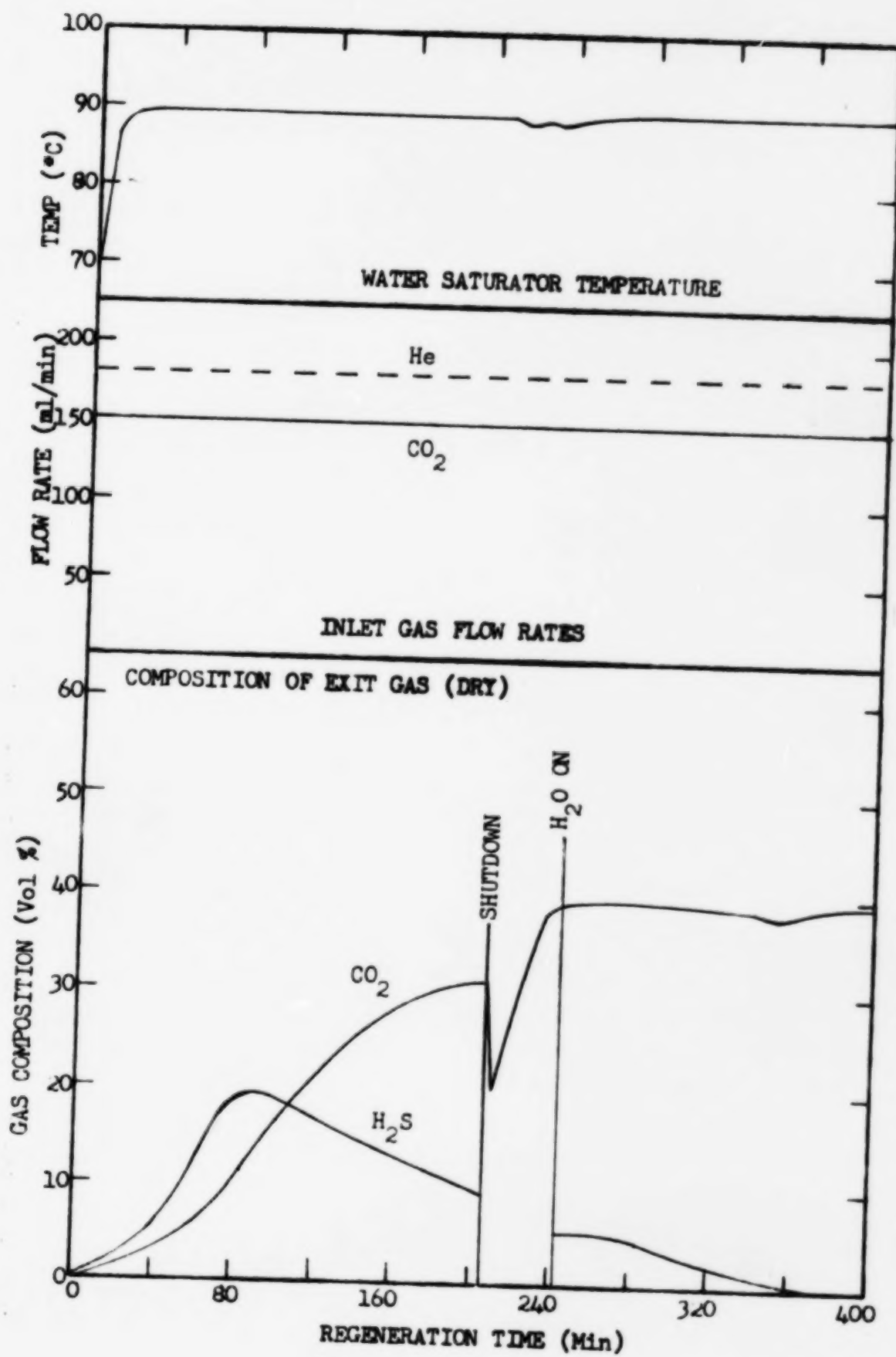


Figure 39. Fourth Regeneration, Cycle Test 5

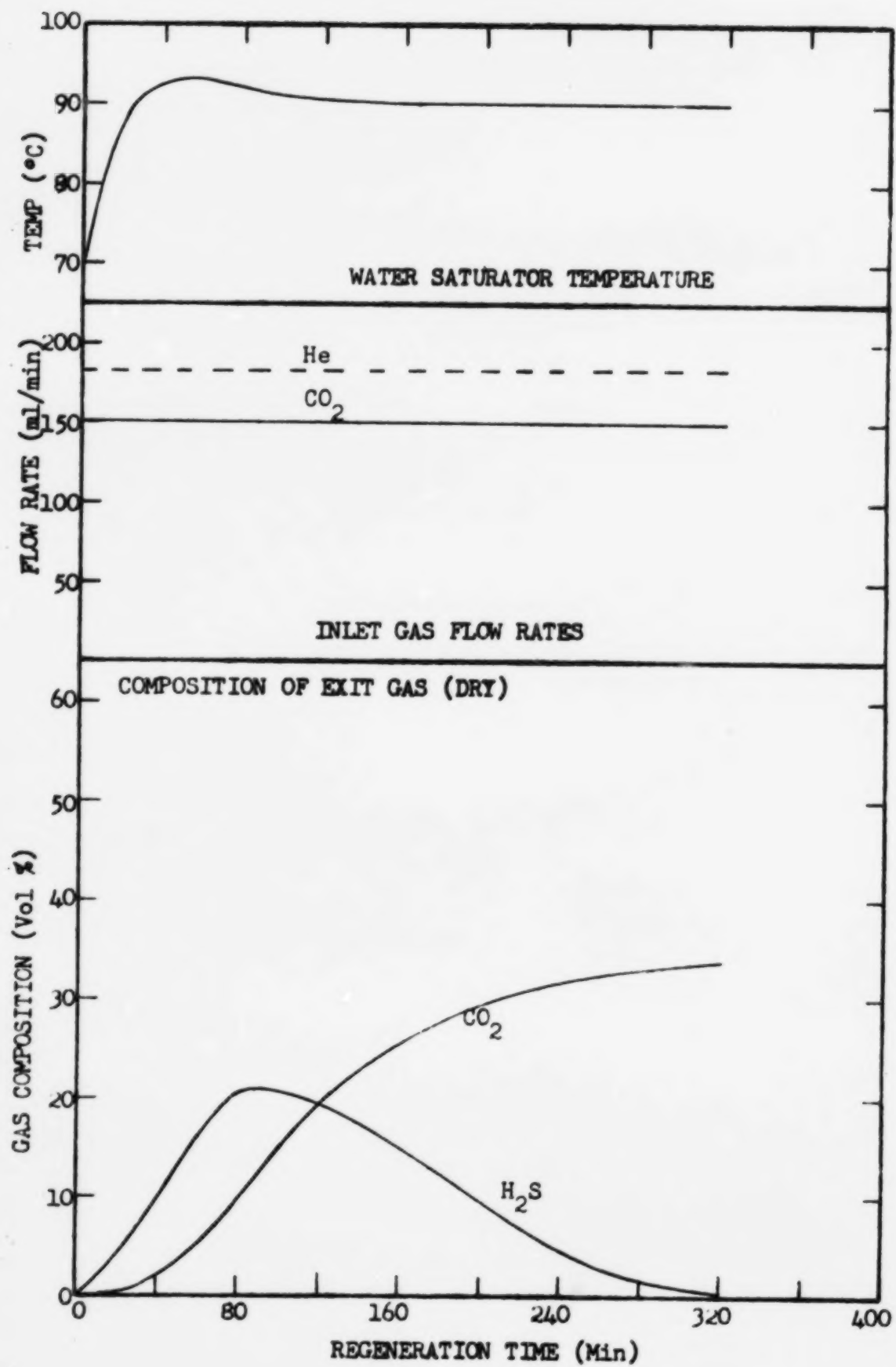


Figure 40. Fifth Regeneration, Cycle Test 5

TABLE 12
Reduction and Regeneration
Times and Sulfur Recovery
for Cycle Test No. 5

Cycle No.	Reduction Time (hr)	Regeneration Time (hr)	Percent Sulfur Recovered
1	(9) ^a	2.4 ^b	48
2	8.5	6.6	108
3	(5.7) ^c	7.4	101
4	13.3	6.8	91
5	10.5	5.0	114

^a Reduced with H₂ saturated with steam at 650°C.

^b Regenerated with a CO₂ flow rate of 0.8 l/min for the first 40 min; CO₂ flow rate reduced to 0.15 l/min.

^c Reduced at 650°C.

TABLE 13

Summary of Data Showing Materials Added and Removed in Cycle Test No. 5

Cycle No.	M ₂ S Added as K ₂ SO ₄ (g)	M ₂ S Removed as H ₂ S During Regeneration (g)	H ₂ O Removed During Reductive (g)	Excess H ₂ O Removed During Regeneration (g)	NaOH Absorbing Solution				Ascarite Weight Gain (g)
					Wt After Rgntn (g)	Wt Gain During Rgntn (g)	Wt % M ₂ CO ₃	Wt % M ₂ S	
1	43.0	20.6	-	70	632.9	43.1	14.5	3.21	6.2
2	39.7	43.0	29.9	126	768.1	42.3	12.0	6.40	5.6
3	39.7	40.2	34.9	103	760.7	60.7	12.2	5.28	9.1
4	39.7	36.2	35.2E	146	631.5	61.8	16.8	5.73	12.1
5	39.7	45.2	33.08	145	779.4	51.2	10.8	5.79	3.7

hydrogen at 600°C, to prepare the sulfide melts. The third regeneration was with a sulfide melt prepared by adding potassium and lithium carbonate and sodium sulfide to the regenerated melt containing the iron catalyst.

The pressure regenerations were carried out in the usual bubble-through reactor. Prior to the start of the regeneration, helium was used as a purge and cover gas to prevent oxidation of the sulfide. In the pressure regeneration tests, the inlet bubbler became plugged with salt as soon as the regeneration was started. These plugs occurred due to slight reductions in pressure when carbon dioxide was introduced into the water saturator; salt flowed up the bubbler into a cool zone and solidified. This difficulty was avoided by starting the regeneration with the water at a lower temperature (~ 90°C) and heating it to the desired temperature after carbon dioxide was passing through the saturator. Also, carbon dioxide was introduced at a slowly increasing rate over a 6-min. period until the desired flow rate was attained. The helium purge rate was likewise decreased to zero slowly over this period.

Table 14 summarizes the data for the preparation of the melts for the regeneration tests. The reductions appeared to proceed at about the expected rate, although none of the reductions were carried to completion.

Part of the data recorded during the cycle test are given in Tables 15 and 16. Table 15 gives the melt compositions before and after regeneration and other data pertinent to the regeneration step. Table 16 gives the weights of the products and reactants collected in the condensers and absorbers in the regeneration steps.

Figures 41-44 show the variation in water saturator temperature, inlet gas flow rates and dry exit gas composition plotted against regeneration time.

TABLE 14
PREPARATION OF SULFIDE MELTS FOR CYCLE TEST NO. 6

Cycle No.	Source of Melt	Treatment	Reduction Conditions (1.4 L/min Hydrogen)		
			Temp (°C)	Reduction Time (hr)	H ₂ O Removed (g)
1	Previously regenerated carbonate melt	Added 30 g M ₂ SO ₄ ^a	600	8	19.9
2	Melt from regeneration No. 1, Cycle 1	Added 45 g M ₂ SO ₄ ^a	600	9.2	28.8
3	Melt from regeneration No. 2, Cycle 2	Added M ₂ S and M ₂ CO ₃ ^b	-	-	-
4	Melt from regeneration No. 3, Cycle 3	Added 75 g M ₂ SO ₄ ^a	600	10.1	45.3

^aAdded equal weights of K₂CO₃, Li₂CO₃, Na₂CO₃, Fe, 1.3 wt %

^bAdded 37 g of K₂CO₃ and Li₂CO₃ and 27.4 g of Na₂S

TABLE 15

Melt Compositions Before and After Pressure Regeneration Tests in Cycle Test No. 6

Cycle No.	Regeneration Conditions			Melt Composition (wt %)				
	Temp (°C)	Pressure (atm)	CO ₂ Flow Rate (ml/min)	Time of Sampling ^a	M ₂ CO ₃	M ₂ S	M ₂ SO ₄	Melt Ht. (in.)
1	500	3	300	i	66.8	13.8	15.9	3.0
				f	82.7	1.8	15.4	2.4
2	500	4.9	390	i	66.6	13.6	-	3.1
				f	89.0	2.2	-	2.4
3	490	4.9	390	i	84.1	11.0	6.7	4.0
				f	92.6	1.3	-	...
4	500	4.9	390	i	73.2	12.6	11.0	5.0
				f	85.3	2.4	-	4.5
				f(F) ^b	87.6	1.1	10.9	4.5

^a i, initial sample prior to regeneration; f, final sample after regeneration. Samples not filtered.

^b f(F), final sample filtered.

TABLE 16

Products and Reactants Collected from Exit Gas During Regeneration Tests in Cycle Test No. 6

Cycle No.	NaOH Adsorbing Solution ^a				Auscrite Wt. Gain (g)	Excess H ₂ O Collected	Total CO ₂ and H ₂ S Collected (g)	
	Weight (g)	Weight Gain (g)	Wt % M ₂ CO ₃	Wt % M ₂ S			CO ₂	H ₂ S
1	762.6	32.8	13.6	3.5	12.5	..	93.5	15.4
	623.7	42.7	16.5	0.94				
2	652.5	(113.2) ^b	16.1	2.8	7.3	46	104.8	16.2
	704.8		16.6	2.4				
3	604.3	47.3	14.1	2.95	5.2	73	86.0	9.7
	519.1	48.2	19.5	0.54				

^a 20 wt% aqueous NaOH solution.

^b Combined weight gain of 2 adsorbers.

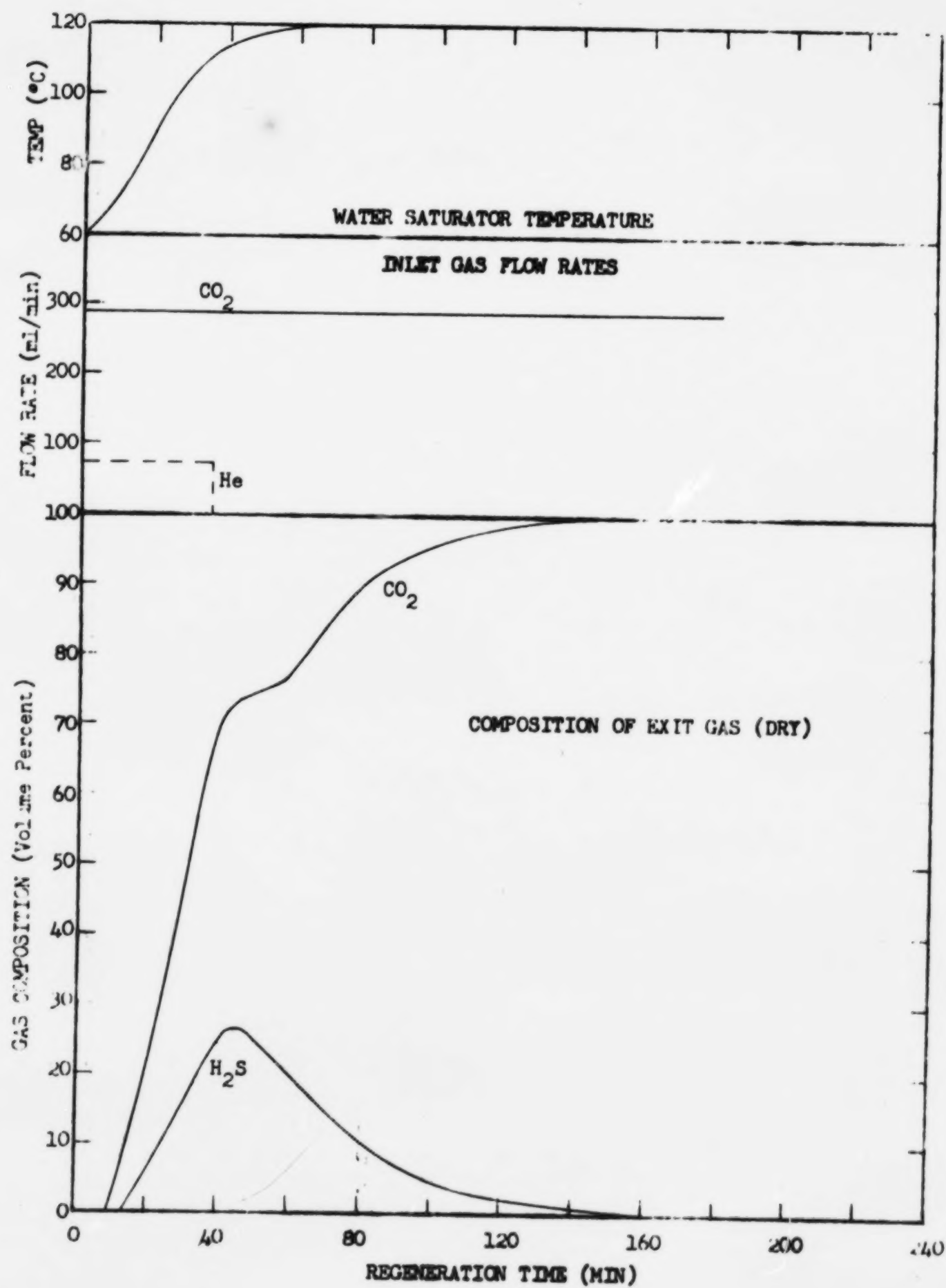


Figure 41. First Regeneration, Cycle Test 6

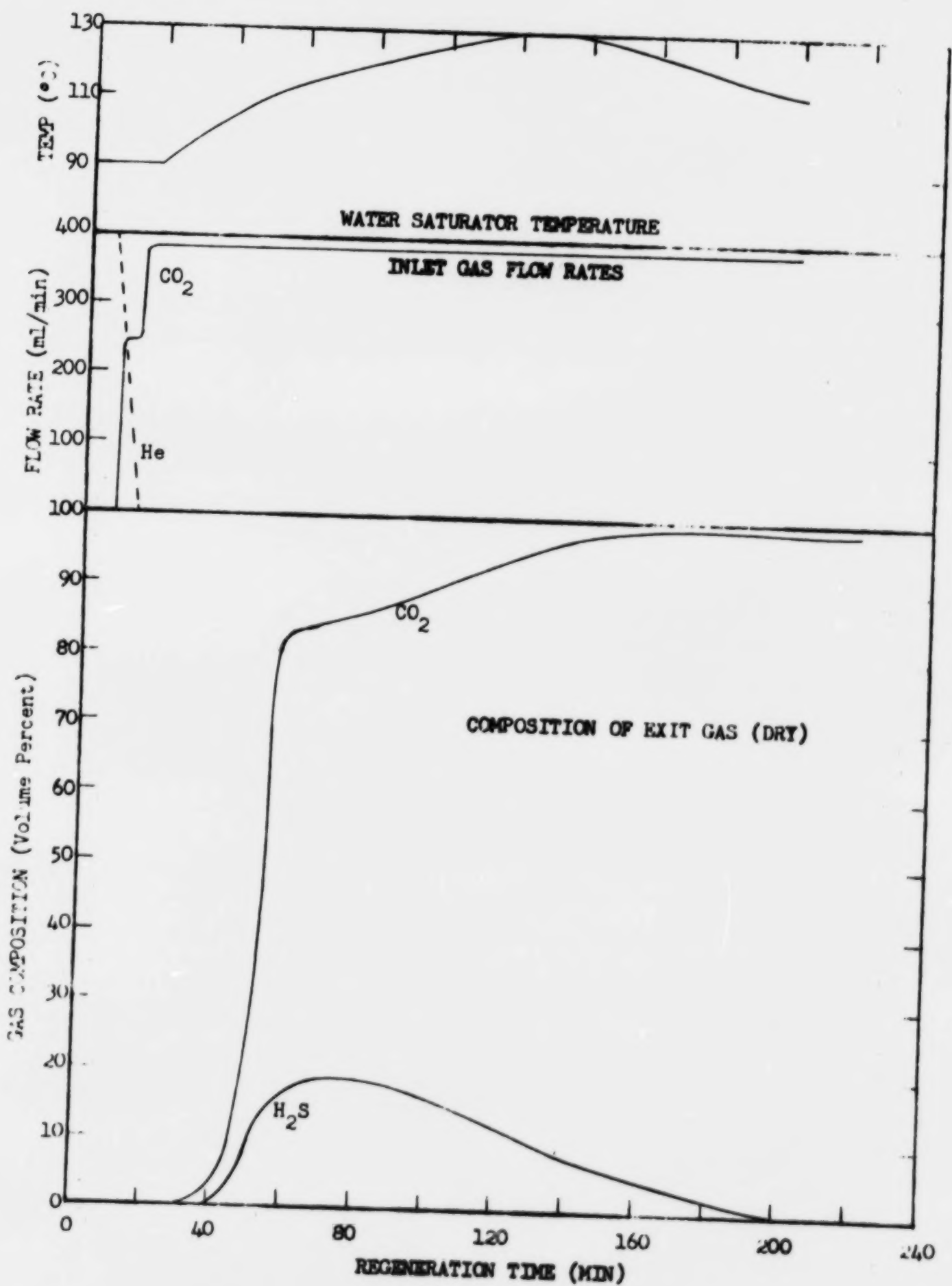


Figure 42. Second Regeneration, Cycle Test 6

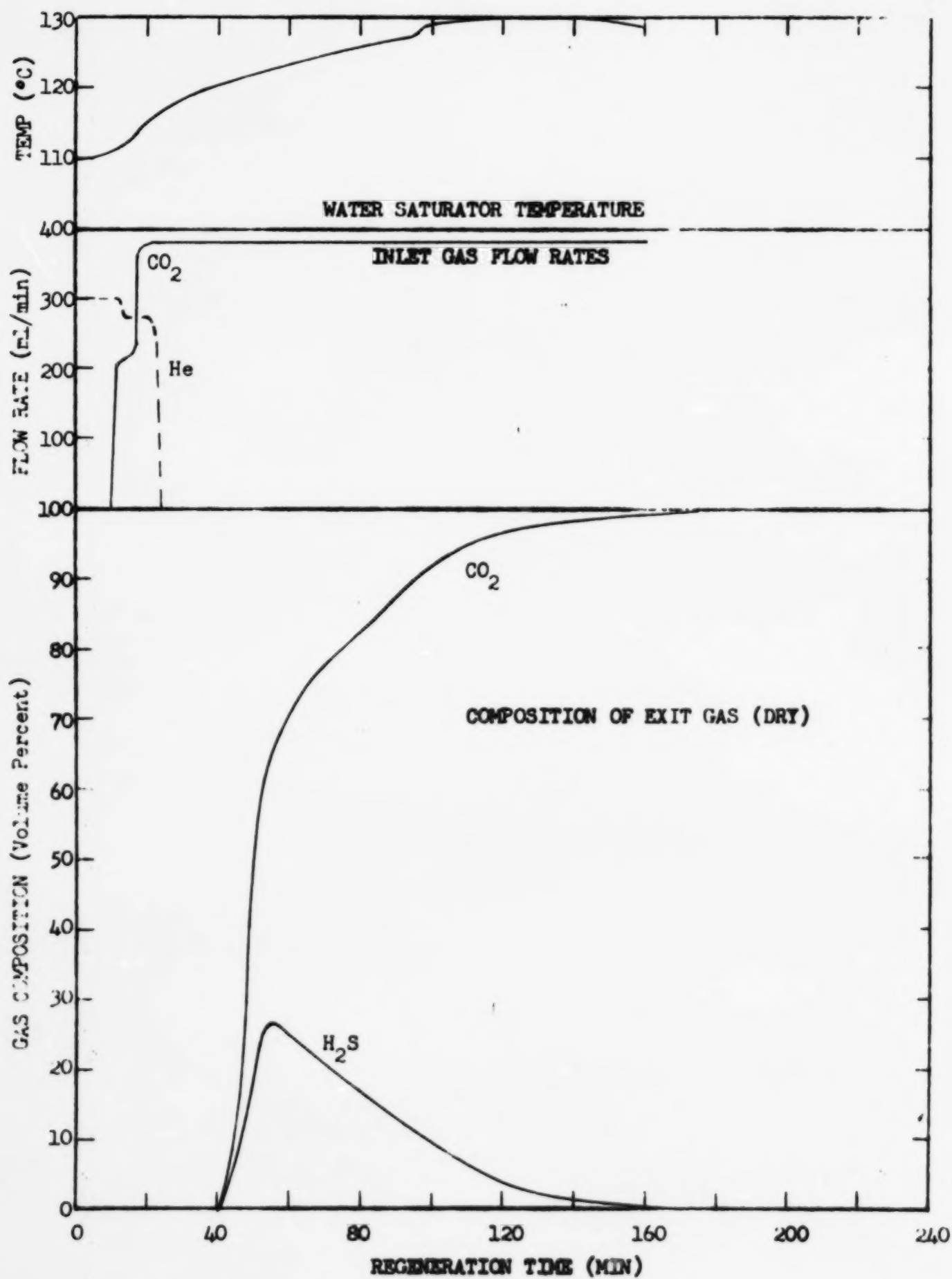


Figure 43. Third Regeneration, Cycle Test 6

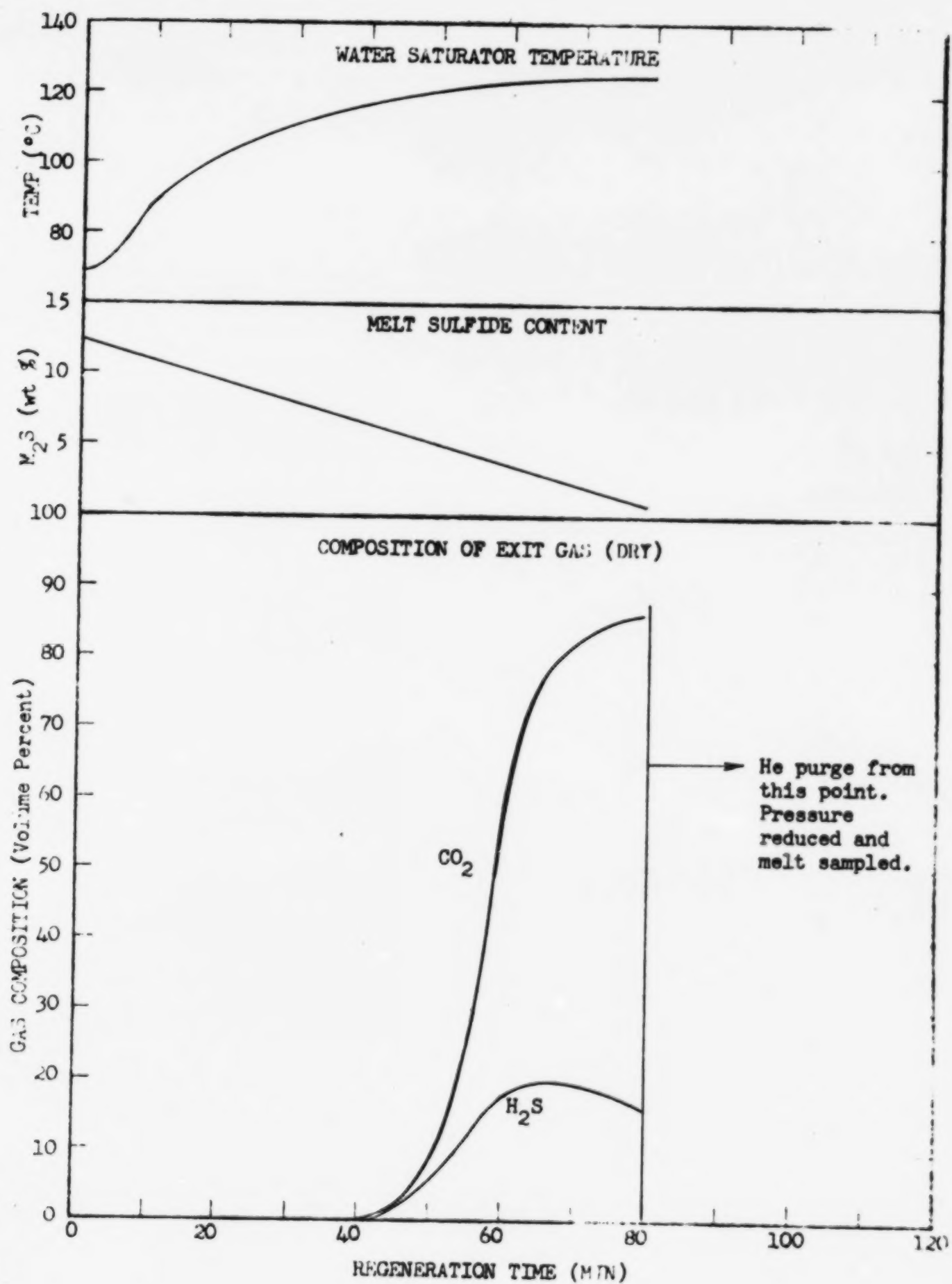


Figure 44. Fourth Regeneration, Cycle Test 6

First of all, the results indicate that the use of higher pressures during regeneration did not promote any unwanted side reactions which would complicate the removal of sulfur. This was indicated by the fact that the sulfide contents (column 7, Table 15) decreased to about the same level as observed in previous regeneration tests at one atmosphere on melts containing iron (Table 11). However, the desired result, an overall increase in conversion or utilization of reactants, was not obtained. This was indicated from data on the amount of excess carbon dioxide and hydrogen sulfide collected from the exit gas for the first three cycles (columns 8 and 9, Table 16). The data show that the mole ratios of excess carbon dioxide to evolved hydrogen sulfide remained at about 4 instead of decreasing to about 2 as a result of the elevated pressure during regeneration. Thus qualitatively, the use of elevated pressure did not produce a greater conversion of reactants to hydrogen sulfide. This conclusion was also reached from an inspection of the exit gas composition data (plotted against time for each cycle in Figures 41-44). The hydrogen sulfide content of the exit gas did not exceed 26 vol% in any of the regeneration steps. Based on the theoretical analysis (section IV), one would have expected the maximum hydrogen sulfide concentration to be about 50%.

The above qualitative observations prompted a detailed analysis of the data from several additional regeneration tests at different pressures. This analysis, discussed in Section IV, resulted in the surprising result that higher carbon dioxide pressures cause a lower conversion of reactants to hydrogen sulfide. The interpretation of this effect as a side reaction between carbon dioxide and sulfide has provided a satisfactory explanation up to this point.

The regenerations were considered complete when the exit gas contained less than 1 vol% H_2S . Regeneration cycle 4 (Figure 44) was stopped prior to this because of a small leak in the exit line. The exit gas flow rate indicated that about 20% of the exit gas was being lost. As shown in Figure 44, the test was stopped when the hydrogen sulfide content of the exit gas was 16%. The melt analysis at this point showed that the sulfide content was about 1 wt% sulfide (in Figure 44, the melt sulfide content is plotted vs. time instead of inlet gas flow rates vs. time). The melt sulfide content was lower than expected at this point. Previously, the regeneration time for a test was based on the time required to reduce the hydrogen sulfide content of the effluent gas to less than 1 vol%. This normally required 4-5 hours in a typical regeneration test using gas flow rates of 150-300 ml/min. However, the regeneration time based on the sulfide content of the melt was considerably shorter than the time based on exit gas composition. The difference is due to the fact that the gas hold up in the system after the gases leave the melt causes several minutes (approximately 20-30 minutes in the elevated pressure tests) to expire before the gases filled the gas sampling chamber. Also, in a typical regeneration, some deposition of salt on the walls could lead to a lingering and slow evolution of hydrogen sulfide. Both of these effects lessen the significance of the regeneration time based on the exit gas hydrogen sulfide content. It is more likely that the regeneration time based on the sulfide content of the melt is the more useful number from the plant design standpoint. It is also more meaningful in the interpretation of the experimental data, especially when high gas flow rates are used in experiments to determine the factors which might be considered rate-limiting in the regeneration reaction. Thus the rate of decrease of sulfide content was used as

the important dependent variable in studying possible rate limitations (see Regeneration Tests 28-31, Table 6 section III and the discussion of these results in section IV).

D. SPECIAL EXPERIMENTS RELATED TO THE REGENERATION PROCESS

During the course of the study of the regeneration process, several special experiments were carried out, to examine in more detail the chemistry in areas where the data obtained in regeneration tests were insufficient for a reliable interpretation. The data from these experiments proved helpful in supporting some of the conclusions arrived at in the analysis of the regeneration test. Table 17 gives a list of the experiments which were carried out.

1. Analysis of Froth Deposits from Regeneration of Sulfide Melts Containing Iron

In the regeneration of reduced melts containing iron, a semi-solid deposit usually formed above the melt line. Samples of these deposits were taken after some regeneration tests were completed and analyzed for carbonate, sulfide and iron. Also, an attempt was made to identify crystalline compounds in the froths by x-ray diffraction analysis. Table 18 gives a summary of the analytical results obtained with several of the froth deposits.

The x-ray diffraction results for the froth from Test 7 indicated that the iron was present in the form of a thio-ferrate (KFeS_2 or possibly as MFeS_2 where M denotes the mixture of Li, Na and K cations). A portion of this froth was ground and washed with water. The insoluble residue remaining after filtration was purple in color and gave an x-ray diffraction pattern containing only KFeS_2 lines. The purple color was consistent with the reported color of KFeS_2 made by fusion of potassium carbonate, iron and sulfur.⁽⁵⁾

TABLE 17
List of Special Experiments
Related to the Regeneration Process

Experiment No.	Title of Experiment
1	Analysis of Froth Deposits Containing Iron from Regeneration Tests 7, 8, 9, 10 and 13.
2	Regeneration of Combined Froth Deposits from Regeneration Tests 7, 8 and 9.
3	Analysis of Tin and German Melts for Sulfide and Total Sulfur.
4	Solubility of Iron(ous) Sulfide and Iron Pyrites in Carbonate Melts.
5	The Absorption of Carbon Dioxide by Melts Containing Sulfides.
6	Reaction of CS ₂ and CO ₂ in Carbonate Melts.

in the froths by x-ray diffraction analysis. Table 18 gives a summary of the analytical results obtained with several of the froth deposits.

TABLE 18
Summary of Analytical Results on Froth Deposits
From Regeneration of Sulfide Melts Containing Iron

Origin ^a of Froth	Froth Composition (wt %)		
	M ₂ CO ₃	M ₂ S	Fe
Test 7	70.1	25.8	5.1 ± 1.0
Test 8	76.2	19.8	9.2
Test 9	79.6	14.2	6.6 ± 1.0

^a See Table 3

2. Attempts to Regenerate Froth Deposits Formed During
Regeneration of Sulfide Melts Containing Iron

The froth deposits from melts after regeneration tests 7, 8 and 9 (composition given in Table 20) were combined ($\sim 100\text{g}$) and an attempt was made to produce hydrogen sulfide by purging the semi-liquid material with carbon dioxide and steam at temperatures from 450 to 600°C. Very little hydrogen sulfide was evolved from the material over a 2-hour period. This behavior was additional evidence that the sulfide in the froth was in some form other than alkali metal sulfide. The sulfide appeared to be in a form which made it unreactive to carbon dioxide and steam.

3. Analysis of Melts from Regeneration Tests of Melts
Containing Tin and Germanium

A low sulfur recovery (5.7% as H_2S) resulted from the regeneration of a sulfide-bearing melt containing 3.4 wt% germanium (Test 5, Table 3). This result was similar to that obtained from a melt containing tin (4.2% recovery, Test #4). The two regeneration tests were also similar in that after treating the melts with carbon dioxide and water, the usual gas chromatographic procedure used for the melt analyses gave low values for the melt sulfide content although only a small amount of hydrogen sulfide was recovered from the exit gases. Because of this problem, the change in sulfur content of the melt from both of these tests was followed by measuring the total sulfur content. The results of the regeneration test on the germanium melt are given in Table 19; they show that only a small amount of the sulfur was removed during regeneration. The corresponding analytical data for the tin melts, in Table 20, also show that most of the sulfur remained in the melt during the attempted regeneration. In both cases, the sulfate content remained essentially unchanged. It was concluded from these data that the sulfide remained

TABLE 19

Melt Compositions During Regeneration of a Sulfide
Melt Containing Germanium

Melt Description	Melt Conditions		Melt Composition (wt %)			
	Temp (°C)	Melt Height (in.)	M ₂ CO ₃	M ₂ S ^a	M ₂ SO ₄	Total Sulfur (as M ₂ SO ₄)
After Reduction	600	3.3	69.4	7.9	14.5	-
Cooled	500	3.3	69.0	7.97	-	26.4
CO ₂ , H ₂ O for 190 min.	500	3.3	80.7	(0.55) ^b	13.84	22.19
CO ₂ , H ₂ O for 297 min.	490	3.4	79.3	(0.12) ^b	13.98	26.36

^a Sulfide analyzed for by usual gas chromatographic method

^b Values in parenthesis are probably low

TABLE 20

Melt Compositions During Regeneration of a Sulfide-
Bearing Melt Containing Tin

Melt Description	Melt Conditions		Melt Composition (wt %)			
	Temp (°C)	Melt Height (in.)	M ₂ CO ₃	M ₂ S	M ₂ SO ₄	Total Sulfur (as M ₂ SO ₄)
After Reduction	600	3.5	74.2	11.6	(~3.0)	-
After CO ₂ for 60 min.	500	3.5	89.8	(4.4) ^b	-	-
After CO ₂ , H ₂ O	500	3.5	97.2	(2.6)	-	12.84
Froth ^a	-	-	65.6	10.3	2.5	24.02
Bulk Salt	-	-	87.9	(3.6)	4.6	19.0

^a Small amount (~ 10g) of deposit probably from insoluble tin compounds.

^b Values in parenthesis are probably low.

unchanged during the test, but that both tin and germanium were converted to the plus four valent state by the action of carbon dioxide and water. In this valent state, both metals could tie up enough sulfide so that the latter could not be converted to hydrogen sulfide under either regeneration conditions or the conditions used for melt analysis for sulfide.

Some possible reactions which could occur, in which both tin and germanium tie up sulfide, are discussed in a later section (section IV). It should be noted that there was some froth-like material produced in the regeneration of tin-containing melts (Table 20). The amount of froth ($\sim 10g$) was much less than observed in the case of melts containing iron. The fact that the melt height did not change during regeneration also indicates that there was only slight foaming during the regeneration. From the total sulfate analysis given in the last column of Table 20, it appears that the sulfide (and maybe tin) might have been concentrated to some extent in the froth. Additional data would be required to understand this. However, since tin and germanium did not appear to be useful as reduction catalysts, further studies of their effect on the regeneration process were not continued.

4. Solubility of Ferrous Sulfide and Iron Pyrites in Carbonate Melts

The solubilities of ferrous sulfide and iron pyrites in molten eutectic carbonate melts were measured. The ferrous sulfide (FeS) was 4-20 mesh tech grade, and the iron pyrites (FeS_2) were technical grade iron pyrites from E. H. Sargent and Co. The solubilities of these two compounds were determined by adding an excess (50g FeS and 15g FeS_2) to 300g of eutectic carbonate in graphite crucibles in an argon atmosphere. The melts were stirred by purging the melts with argon through a graphite bubbler. The melts were

heated and stirred for several hours at a constant temperature before filtered and unfiltered melt samples were taken. The melt samples were analyzed for sulfide and iron by the usual methods. The analytical results are shown in Tables 21 and 22. X-ray diffraction patterns were obtained for several samples, including the iron-sulfur compounds. The analysis of the x-ray patterns are summarized in Table 23. The x-ray diffractions of both ferrous sulfide and iron pyrites remained unchanged after heating the latter compounds at 500°C for periods of time, and therefore showed no signs of undergoing thermal decomposition. However, the matrix formed by heating both compounds with carbonate eutectic showed evidence of other iron-containing compounds; e.g., KFeS_2 . This was evidence that the latter types of compound are more stable than either ferrous sulfide or pyrite in a molten carbonate environment.

Neither ferrous sulfide or iron pyrite appear to be appreciably soluble in the eutectic carbonate melt at 500 to 600°C. Both compounds appear to be altered by heating in carbonate melt. This is evidenced by the fact that (1) the sulfide can be analyzed for by the usual technique and (2) x-ray diffraction patterns of carbonate-iron compound fusions show little sign of the original iron compound. The latter patterns are similar to those obtained on iron-rich froths obtained in regeneration tests, in that they show lines attributed to KFeS_2 . There did not appear to be as much KFeS_2 in the "synthetic" froths.

The addition of sodium sulfide to the carbonate melt saturated with ferrous sulfide enhanced the solubility of ferrous sulfide as shown by sample 10, Table 21. Thus, when the soluble sulfide content of the melt was 10.9 wt%, the soluble iron content was 1.2 wt%. These values are in good agreement with the results obtained during a regeneration experiment in which a 12.3 wt% sulfide melt contained 0.7 wt% soluble iron.

TABLE 21

Solubility of Iron (ous) Sulfide in Eutectic Molten Carbonate and in Molten Sulfide-Bearing Melts

Sample No.	Temp of Melt (°C)	Method of Sampling ^a	Melt Composition (wt %)		
			M ₂ CO ₃	M ₂ S	Fe
1	500	U	99.03	2.2 ^b	4.5
2	500	F	100.1	0.08	0.33
3	640	U	91.9	1.55	3.5
4	640	F	100.1	0	0.36
(Cooled)					
5	500	U	96.4	0.64	2.1
6	500	F	101.8	0	0.04
Added 15 g Na ₂ S					
7	500	U	90.3	8.7	2.2
8	500	F	100.0	1.3	0.08
Added 15 g Na ₂ S					
9	500	U	81.3	19.5	8.2
10	500	F	92	10.9	1.2
Treated Melt with CO ₂ (150 ml/min) for 90 min.)					
11	500	U	89.8	10.2	-
12	500	F	96.4	4.2	-

^a U = unfiltered melt samples; F = melt samples filtered through 35 μ pore size sintered stainless steel filters.

^b No sulfide was found in iron (ous) sulfide, 4-20 mesh, by the same technique used for analyzing melt samples.

TABLE 22

Solubility of Iron Pyrite in Eutectic Molten Carbonate

Sample No.	Temp of Melt (°C)	Method of Sampling	Melt Composition (wt %)		
			M ₂ CO ₃	M ₂ S	Fe
1	500	U	86.3	3.4 ^b	5.8
2	500	F	99.8	0	0.07
3	580	U	92.5	7.6	2.5
4	580	F	100.0	0	0.045

^a U = unfiltered samples; F = melt filtered through 35 μ sintered stainless steel filter.

^b No sulfide was found in iron pyrites when analyzed by the same technique used for analyzing melt samples.

TABLE 23

Summary of X-ray Diffraction Analysis of Iron Sulfur Compounds Heated with and Without Eutectic Carbonate

Initial Iron Sulfur Compound	Treatment Prior to Obtaining X-ray Diffraction Pattern	Interpretation of X-ray Diffraction Pattern
FeS ^a	Heated at 500°C for 12 hr in argon	Troilite (FeS)
FeS	Heated with M ₂ (S, CO ₃) at 500°C, cooled sample 9, Table 5	Probably some KFeS ₂ and probably some FeS
FeS ₂ ^b	As is	Mixture of iron pyrite and alpha quartz
	Heated at 500°C for 12 hr in argon	Mixture of iron pyrite and alpha quartz
FeS ₂	Heated with M ₂ CO ₃ at 500°C (sample 1, Table 6)	Pattern similar to iron sulfur deposits obtained from regeneration tests except less KFeS ₂

^a Iron (ous) sulfide, 4-20 mesh, tech.

^b Iron pyrites (tech.).

Sodium sulfide was added in two 15g increments. After the first addition, it was noted that the soluble sulfide content of the melt remained low (1.3 wt%, column 5, Table 21). This could be interpreted as an interaction of sulfide with ferrous sulfide to form an insoluble compound, e.g., NaFeS_2 . An appreciable amount of soluble sulfide was found in the melt only after a second 15g quantity of sodium sulfide had been added. The 90-minute treatment of the melt after the addition of sodium sulfide produced a small amount of carbonyl sulfide and hydrogen sulfide. However, the sulfide content of the melt decreased much more (from 10.9 to 4.2 wt% M_2S) than could be accounted for by the amount of carbonyl sulfide and hydrogen sulfide evolved. The decrease may have resulted either from the precipitation of iron thiocarbonates or the oxidation of ferrous to ferric iron and the precipitation of the ferric iron as a thioferrate (MFeS_2). The overall results indicate that iron sulfide precipitate which forms during regeneration is probably not ferrous sulfide or iron pyrites.

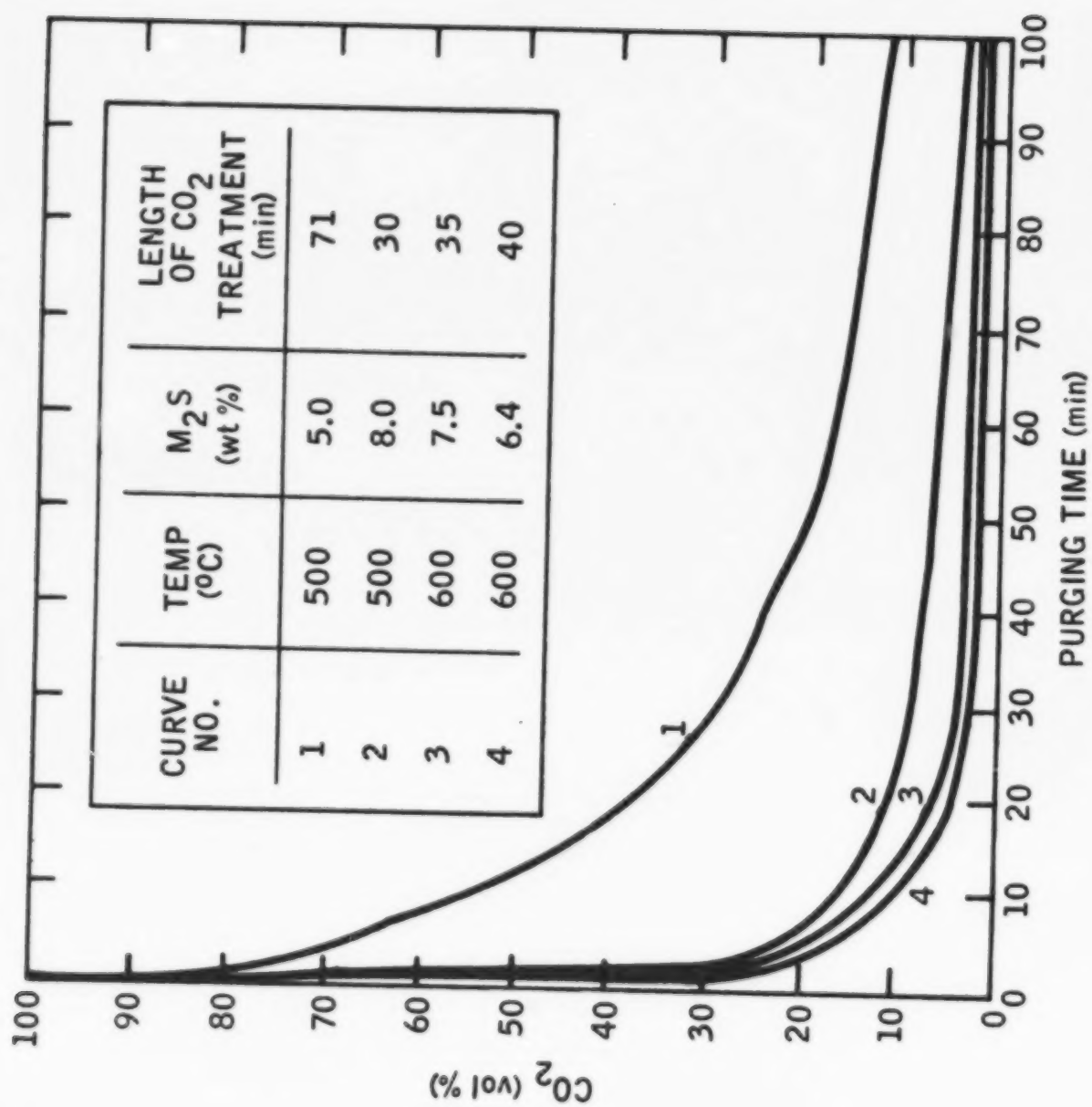
5. The Absorption of Carbon Dioxide by Melts Containing Sulfides

Carbon dioxide-saturated melts were prepared by bubbling carbon dioxide through sulfide-bearing melts. The experiments were carried out in the same apparatus used for the regeneration experiments, with sulfide melts prepared the same way. The system was purged with helium (200 ml/min) while the melt was being heated to the test temperature. When the desired temperature was reached (500°C or 600°C), the melt was purged with carbon dioxide for periods of 30 to 40 min. (400 ml/min at 1 atm pressure). One melt was purged with carbon dioxide for a period of 71 min. After the carbon dioxide flow was stopped, the melt was immediately purged with helium at 400 ml/min for a 2 to 3-hr period, until the carbon dioxide content of the effluent was less than

1 vol%. Figure 45 shows the volume percent of carbon dioxide in the effluent plotted versus time during the helium purge. Three different melts were studied. The first two (curves 1 and 2, Figure 45) were treated with carbon dioxide at 500°C. The third melt was treated with carbon dioxide two times at 600°C. The second treatment was started as soon as the absorbed carbon dioxide from the first treatment had been removed. Curve 3 shows the effluent gas composition after the first treatment. Curve 4 shows the effluent gas composition after the second treatment.

The total carbon dioxide removed from the melt during the helium purge was determined by absorption in ascarite. A second method was also used to determine the amount of carbon dioxide evolved. In the second method the flow rate of the carbon dioxide effluent was calculated from the effluent gas composition data given in Figure 45. The flow rate of carbon dioxide was then plotted against time for the melts studied, and the area under the curve was measured with a planimeter to estimate the amount of carbon dioxide absorbed by the sulfide melt. On the average, the amount of carbon dioxide determined by the effluent gas composition data was somewhat smaller (10-20%) than the amount determined by trapping in ascarite.

The amount of carbon dioxide absorbed by sulfide melts ranged from 0.5 to 1.5 moles of carbon dioxide per mole of sulfide on the basis of these preliminary tests. The amount appeared to depend upon the duration of time used to saturate the melts, even though excess amounts of carbon dioxide were used in the treatment. This may indicate that the absorption is kinetically limited. This could be important in the regeneration process. It suggests that if the regeneration step were carried out rapidly, at high ratios of regeneration gas flow rate to melt volume, then the carbon dioxide

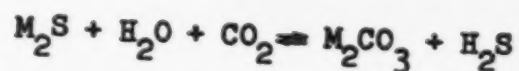


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Figure 45. Release of Carbon Dioxide by Melts

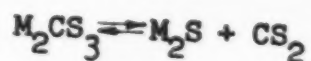
pressure effect would be less pronounced. Thus it may ultimately be possible to regenerate at higher pressures and to obtain greater conversion using high input gas feed rates.

The fact that a substantial portion (66%) of the carbon dioxide absorbed by sulfide melts can be removed by purging the saturated melts with helium shows that the absorption is to a great extent, a reversible reaction. This also supports the chemical interpretation (formation of thiocarbonates, see section IV) of the carbon dioxide pressure effect on the regeneration process, since all of the sulfide can be removed through the reaction,



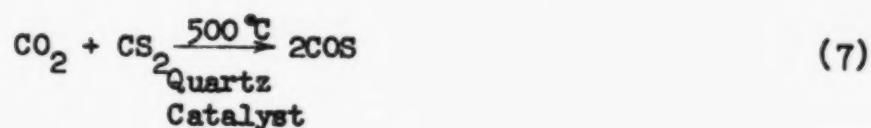
6. Interaction of Carbon Disulfide and Carbon Dioxide in Carbonate Melts

The tentative explanation for the absorption of carbon dioxide by sulfide melts is that carbon dioxide interacts with sulfide to form a series of thiocarbonates in the molten carbonate. Pure solid alkali metal thiocarbonates undergo thermal decomposition in the 200-400°C temperature range;⁽⁶⁾ however, the existence of thiocarbonate ions in carbonate melts above 400°C cannot be ruled out. If the thiocarbonate ion, CS_3^- , were formed, one might expect to find carbon disulfide in the effluent gas, since trithiocarbonates decompose under some conditions by the reaction,

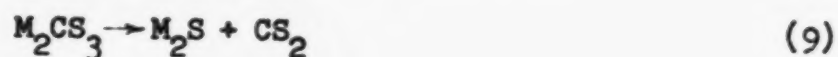
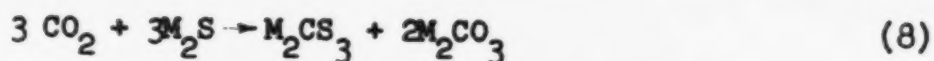


However, cold trapping and gas chromatograph analysis showed that carbon disulfide was not present in the effluent gases.

One of the methods for preparing carbonyl sulfide is the reaction,



However, even if carbon disulfide was produced during the carbon dioxide treatment of a sulfide melt, it might have reacted with carbon dioxide according to reaction 10 below. Thus the sequence of reactions:



could account for the presence of carbonyl sulfide in the effluent during the carbon dioxide treatment of a sulfide-bearing melt. In order to determine if reaction (10) goes to completion under the conditions existing in the regeneration step, the following experiment was carried out. Carbon dioxide saturated with carbon disulfide (20-30 vol percent CS_2) was bubbled through pure eutectic carbonate melt at 500°C for a period of 70 minutes. During the experiment, the effluent gas composition was determined periodically. The effluent gas consisted of carbon dioxide, carbonyl sulfide and probably carbon monoxide. During the test the carbonyl sulfide concentration gradually increased from about 1 vol percent to about 4 vol percent at the end of the test. The melt sulfide content at the end of the test amounted to 3.2 wt%.

Based on the material balance for sulfur, the disposition of the carbon disulfide introduced (0.076 moles) in the feed gas was as follows:

absorbed in carbonate melt	58%
converted to COS	20%
collected in effluent cold trap	4%
accounted for	82%
unaccounted for	18%

Thus if the calculations are based upon the amount of carbon disulfide introduced, the results indicate that 58% was converted to sulfide in the melt, 20% was converted to carbonyl sulfide, 4% was recovered from the effluent and 18% was lost. It is probable that the last number represents the experimental error involved in making the material balance. The main conclusions from the results are:

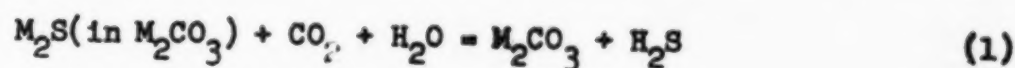
a) Carbon disulfide or the carbonyl sulfide product of its reaction with carbon dioxide are absorbed in appreciable quantities by the molten carbonate melt.

b) If carbon disulfide were produced in the treatment of a sulfide melt with carbon dioxide, it should not be observed in significant quantities in the effluent gases.

IV. DISCUSSION

A. THEORETICAL ANALYSIS OF THE REGENERATION REACTION

A theoretical analysis was carried out to show the effect of system pressure, and of changes in the inlet ratio of carbon dioxide to water vapor, upon the effluent gas composition. This analysis was made with the assumption that the regeneration reaction



is the only reaction which takes place and that all reactants behave ideally. The interaction of carbon dioxide with sulfide melts was not considered in this analysis because of lack of sufficient data about the reaction. As it later turned out, the carbon dioxide interacted with the sulfide to such an extent that the pressure effect was opposite that expected from the analysis.

The effective equilibrium constant for the regeneration reaction is defined as

$$K_e = \frac{X_{M_2CO_3} P_{H_2S}}{X_{M_2S} P_{CO_2} P_{H_2O}} \quad (\text{atm}^{-1}) \quad (11)$$

where X is the mole fraction and p_i is the partial pressure in atmospheres of gas i where i is either H_2S , CO_2 or H_2O . The effects of changes in the variables, X_{M_2S} , temperature, pressure and CO_2/H_2O ratio were examined theoretically, beginning with equation (11).

The following expression was derived and used for calculating the partial pressure of H_2S in the effluent gas when a melt is reacted with a 1:1 mole ratio of CO_2 and H_2O :

$$P_{H_2S} = \frac{[2PK(X/1-X)+1] - \sqrt{4K(X/1-X)P+1}}{2K(X/1-X)} \quad (12)$$

where X = mole fraction of M_2S and $1-X = X_{M_2CO_3}$

P = inlet partial pressure of $CO_2 = P_{H_2O}$ in atmospheres

K = equilibrium constant for the regeneration reaction (1)

The extent of reaction or conversion is defined as

$$\frac{P_{H_2S} \times 100}{P} = \text{percent conversion of either } CO_2 \text{ or } H_2O \text{ to } H_2S;$$

and percent of H_2S in the dry effluent gas if
there is no inert carrier gas.

Equation (12) was used to calculate the equilibrium pressure of hydrogen sulfide as a function of the sulfide concentration (X_{M_2S}) at 0.8 and 5 atm total pressure of the inlet equimolar mixture of carbon dioxide and steam. Two values (10 and 18 atm⁻¹) were used for the equilibrium constant. The first value, 10, was the experimentally determined value at 500°C. The second value, 18, was the extrapolated value for the regeneration reaction at 420°C, assuming a heat of regeneration of -26 kcal/mole.

For an inlet pressure of 0.8 atm, Figure 46 shows the calculated volume % of hydrogen sulfide in the dry effluent gas (carbon dioxide plus hydrogen sulfide) plotted against the sulfide concentration of the carbonate melt. The upper curve is for a K value of 18 and the lower curve is for a K value of 10.

Figure 47 shows similar plots to Figure 46 for a total inlet regeneration gas pressure of 5 atm. Both Figures show that the hydrogen sulfide content of the effluent begins to drop rapidly when the sulfide concentration drops below 0.02 mole fraction (1.4 wt% sulfide). The pressure of hydrogen sulfide in the dry effluent gas in equilibrium with a melt containing 0.002 mole fraction sulfide (0.14 wt% sulfide) can be read from these plots. The batch regeneration studies (tests 1-21, Table 3) had been considered complete when the sulfide content of the melt was 0.1 to 0.2 wt%. From Figure 46, the amount of hydrogen sulfide in a dry effluent gas in equilibrium with a melt of 0.14 wt% sulfide ($X_{M_2S} = 0.2$) is 1 vol% at 0.8 atm. For the 5 atm test

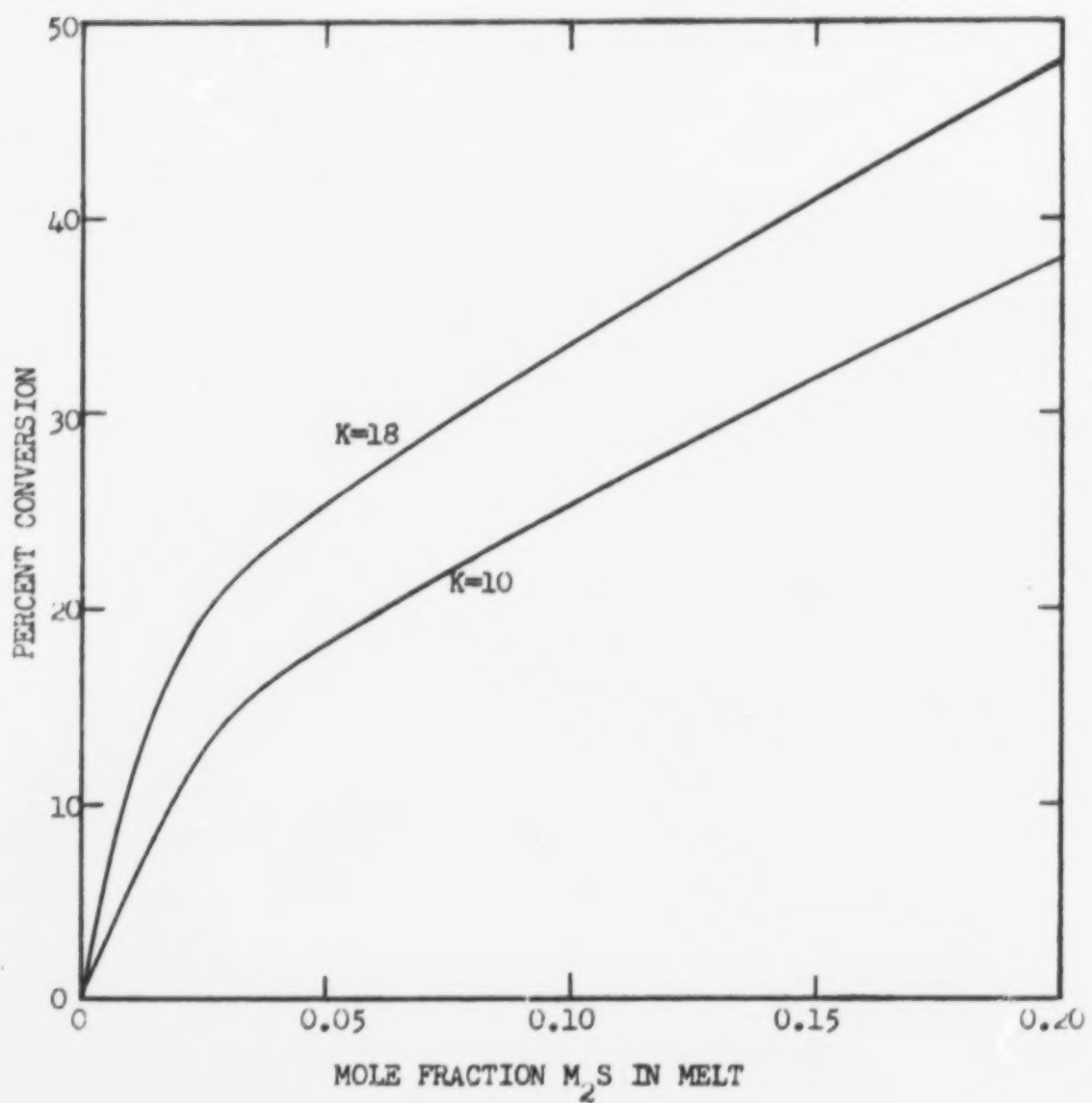


Figure 46. Effect of Melt Sulfide Content on Conversion to Hydrogen Sulfide at 0.8 Atm Pressure

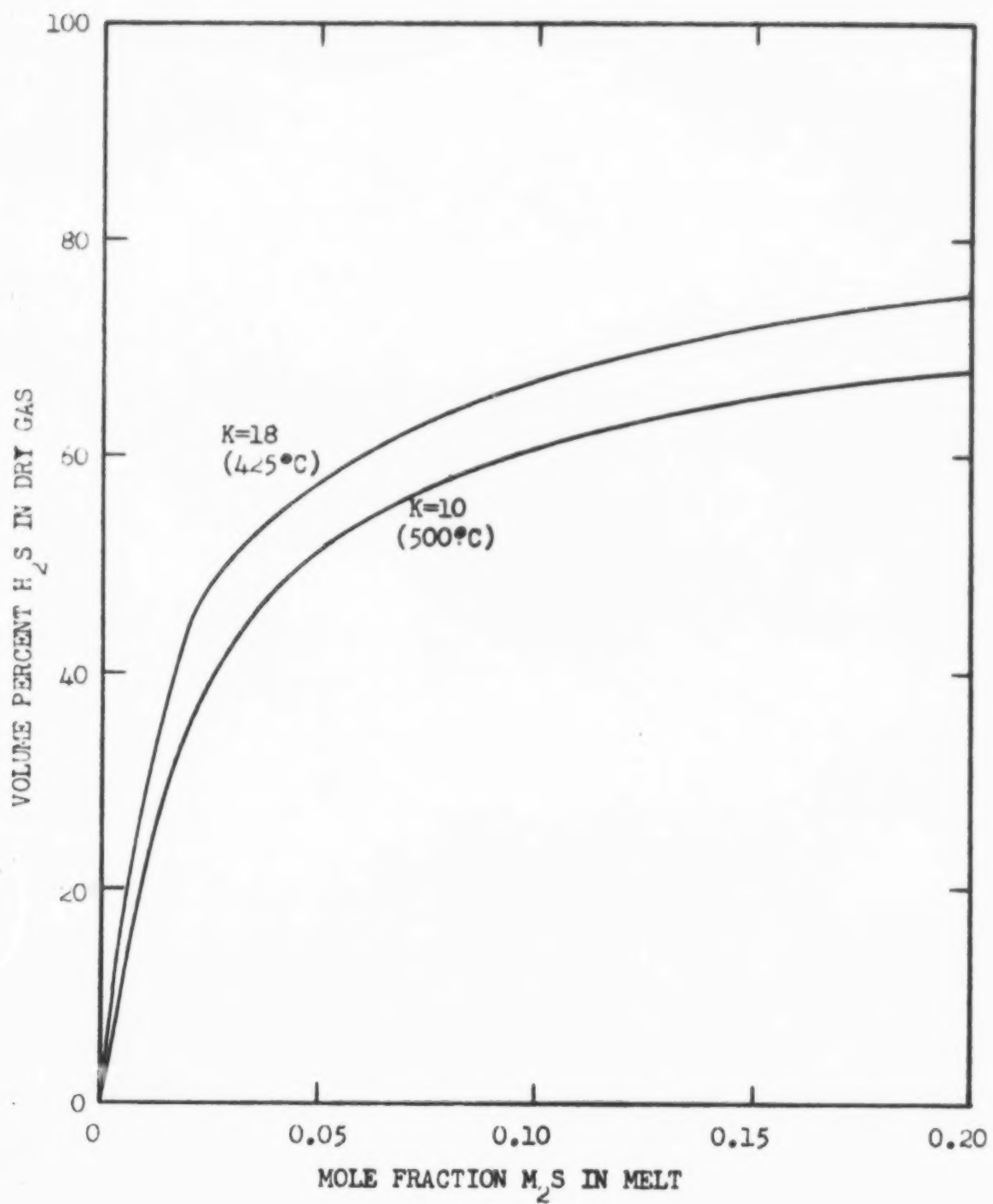


Figure 47. Effect of Melt Sulfide Content on Conversion to Hydrogen Sulfide at 5 Atm Pressure

(Figure 47), the hydrogen sulfide content is 5 vol% for the same sulfide concentration.

Effect of Varying the Carbon Dioxide/Water Vapor Inlet Gas Ratio

The effect of varying the carbon dioxide/water vapor mole ratio on the effluent gas composition and on the amount of conversion of reactants to hydrogen sulfide was examined. Figure 48 shows the total conversion of reactants to hydrogen sulfide plotted as a function of the percent of steam in the inlet stream. The complete curve was calculated for a regeneration gas mixture of carbon dioxide and water vapor at a total inlet pressure of 0.8 atm and a melt containing 7.4 wt% sulfide. The top curve, calculated only for the 50/50 carbon dioxide-water vapor mixture, is for a 15.25 wt% sulfide (20 mole percent) melt.

Figure 49 shows the effect of the feed gas carbon dioxide/water vapor ratio on the effluent gas composition, on a ternary chart. The base line represents the composition of the feed gas to the regenerator. The intersection of the line from the base and the curve showing the sulfide content of the melt gives the composition of the effluent gas. For example, the composition of the effluent for a 25% water vapor-75% carbon dioxide feed mixture in contact with a melt containing 0.2 mole fraction sulfide is 18 vol% hydrogen sulfide, 11.5 vol% water vapor and 70.5 vol% carbon dioxide (point A on the chart). Point B represents the effluent composition if the melt were pure sulfide (sulfide presumably would not be molten in the real case). In this case the effluent would consist of carbon dioxide and hydrogen sulfide and very little moisture. Point C on the chart would correspond to an effluent composition from a pure sulfide melt if the feed gas contained an excess amount of water to carbon dioxide (75%-25%). In this case, the effluent would

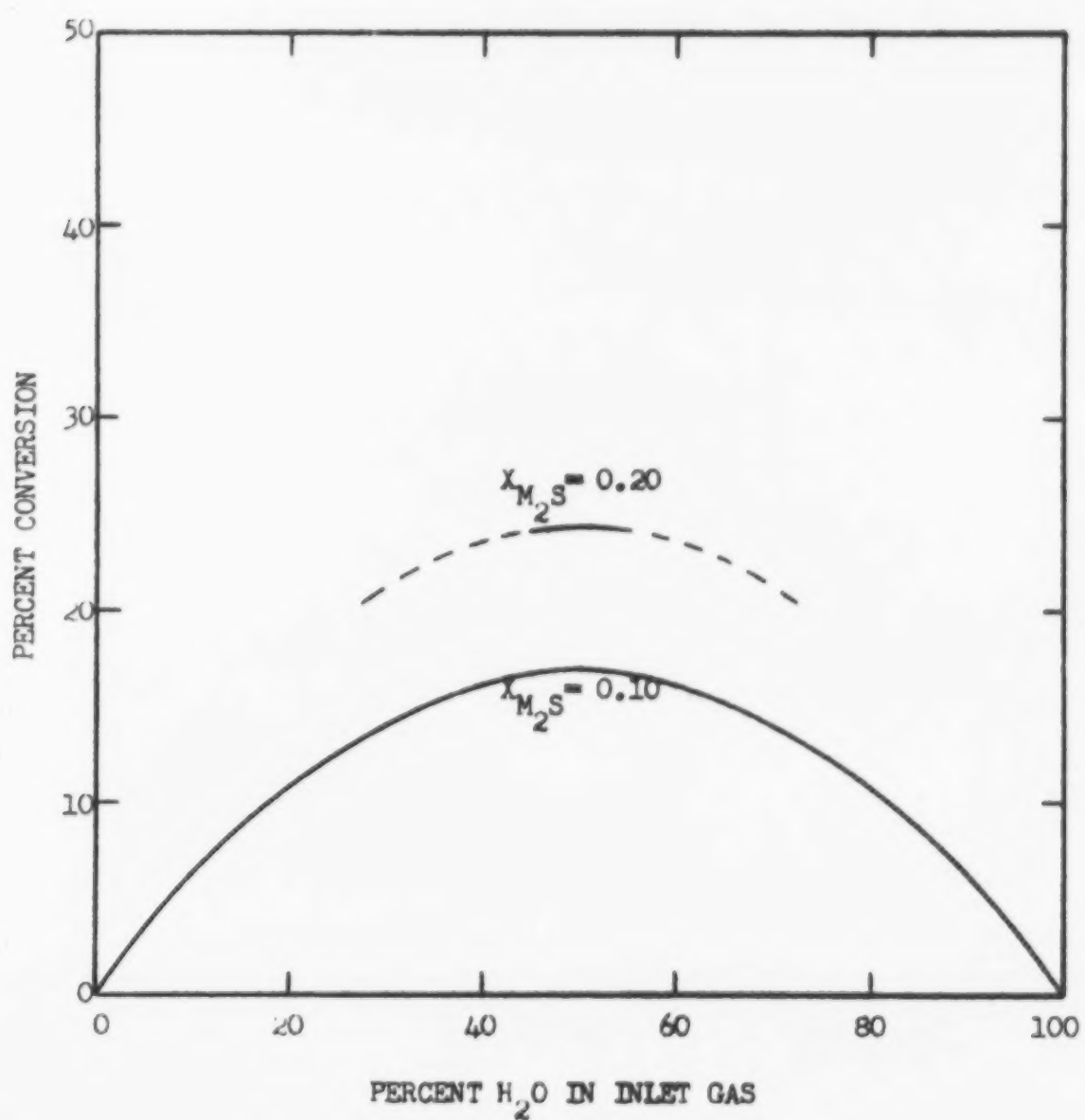


Figure 48. Effect of Carbon Dioxide to Water Ratio on Conversion to Hydrogen Sulfide

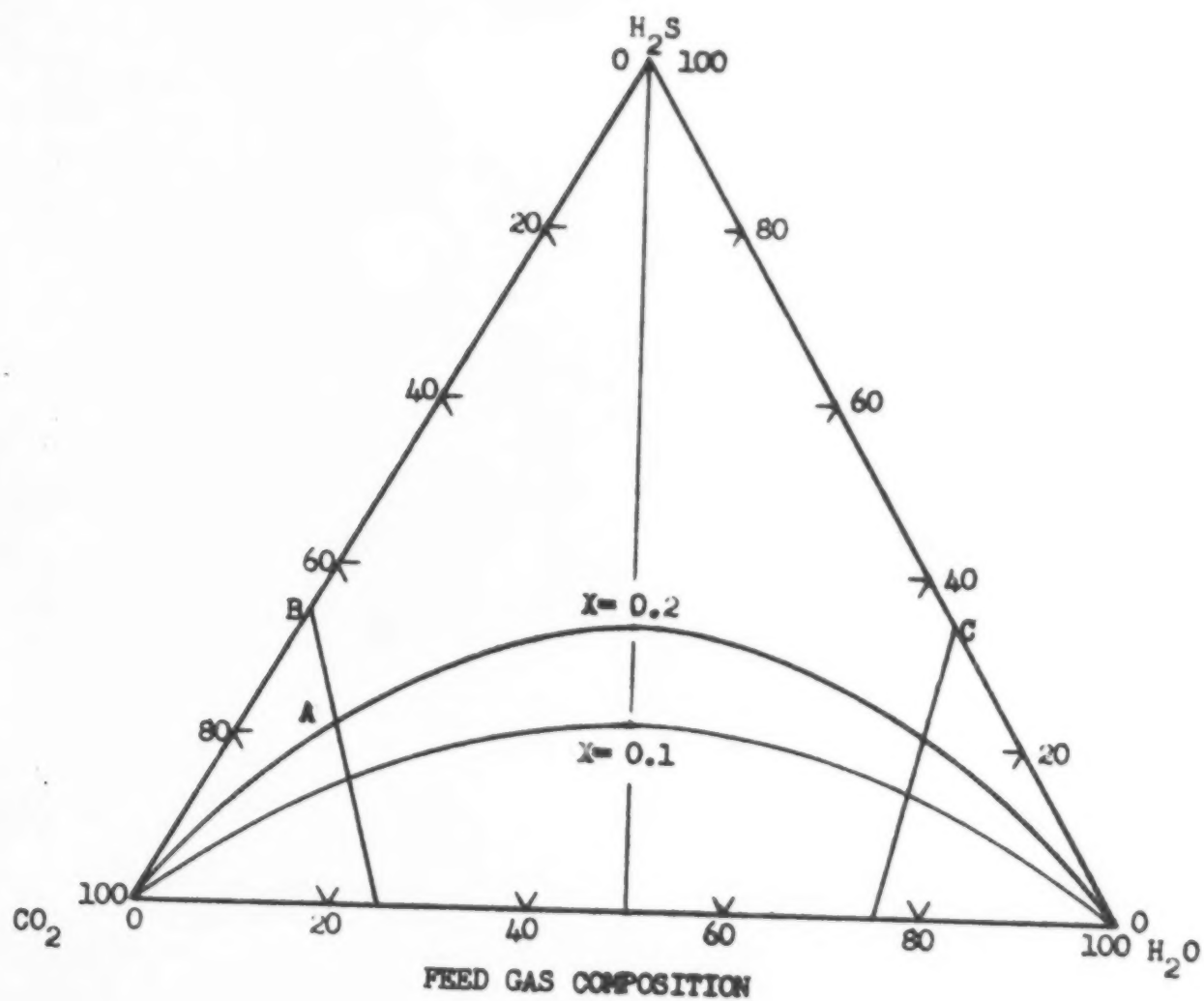
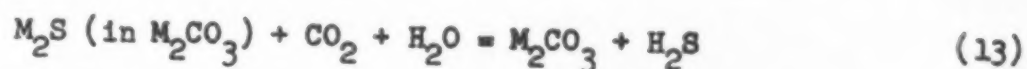


Figure 49. Ternary Regeneration Diagram

contain very little carbon dioxide. This chart serves to provide an overall picture of the effects of inlet gas and melt composition upon the composition of the effluent gas.

B. METHOD OF CALCULATING EFFECTIVE EQUILIBRIUM CONSTANTS FROM REGENERATION TEST DATA

The effective equilibrium constants for the reaction:



can be calculated from the experimental data of the regeneration tests at any given time from the start of the regeneration reaction to the completion of the tests, using equation (11) and the recorded experimental data. The concentrations of the salt components were calculated from the gas chromatographic data which gave the amount of hydrogen sulfide evolved and from the initial and final melt sulfide concentrations. The areas of the plots of volume percent hydrogen sulfide in the exit gas vs time were integrated with a planimeter to determine the percent of hydrogen sulfide generated within a given time interval. From these data, the amount of sulfide remaining in the melt could be determined at any given time. The percent of carbon dioxide and water vapor converted to hydrogen sulfide was determined from the gas chromatograph data of the exit gas. The partial pressure of carbon dioxide in the inlet gas was calculated from the vapor pressure of water at the water saturator temperature:

$$P_{in}(CO_2) = 1 - P_{in}(H_2O) \text{ (v.p. at water saturator temperature)} \quad (14)$$

The partial pressure of the products and reactants were determined as follows:

$$P_{CO_2} = \frac{P_{in}(CO_2) - P_{in}(CO_2) \times (\% CO_2 \text{ converted})}{\text{Corr. factor}} \quad (15)$$

$$P_{H_2S} = \frac{P_{in}(CO_2) \times (\% CO_2 \text{ converted})}{\text{Corr. factor}} \quad (16)$$

$$P_{H_2O} = \frac{P_{in}(H_2O) - P_{in}(CO_2) \times (\% CO_2 \text{ converted})}{\text{Corr. factor}} \quad (17)$$

where $P_{CO_2} + P_{H_2S} + P_{H_2O} = P_T$, total pressure of reactants (18)

$$\text{and Corr. factor} = \frac{P_{in}(CO_2) + P_{in}(H_2O) - P_{in}(CO_2) \times (\% CO_2 \text{ converted})}{P_T} \quad (19)$$

The correction factor (equation 19) adjusts the partial pressures so that the total pressure (P_T) is equal to the experimental pressure of the system.

C. EFFECTIVE EQUILIBRIUM CONSTANTS CALCULATED FROM REGENERATION TEST DATA

A quantitative evaluation of the regeneration data from the several regeneration tests was made. This evaluation consisted of calculating the effective equilibrium constants for the regeneration reaction at various stages of completeness during the regeneration according to the procedure outlined in part (B).

The equilibrium constants calculated in the above manner for two tests (Reg. Tests 25 and 27, Table 6) carried out at 1 atm pressure are shown in Figure 50. Figure 51 shows a similar plot for tests 24, 25 and 26 (Table 6) (5, 1 and 0.4 atm reactant pressure, respectively). Figure 52 shows a plot of K vs X_{M_2S} for the test with slow inlet gas feed rate at 1 atm (Test 28, Table 6).

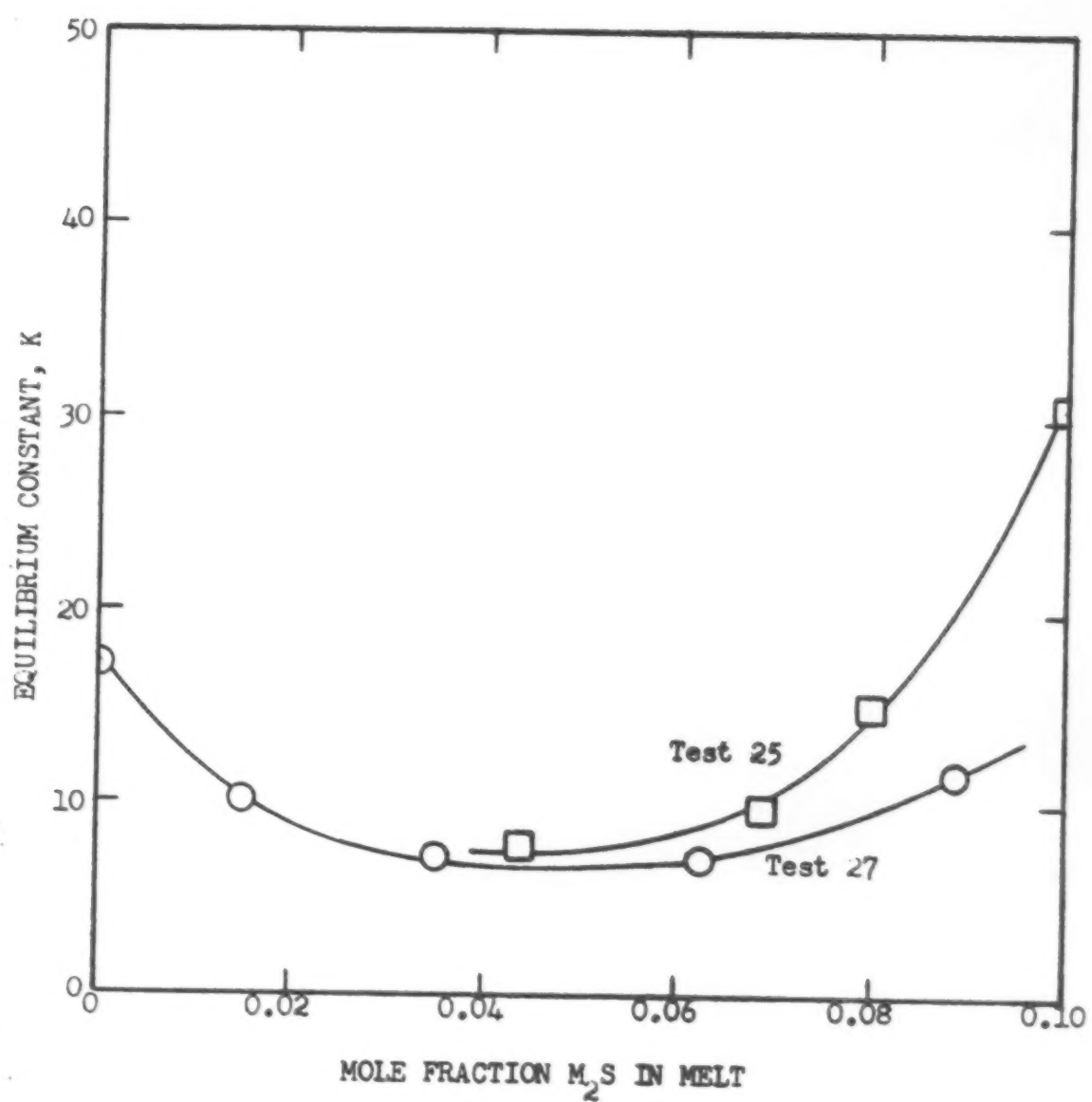
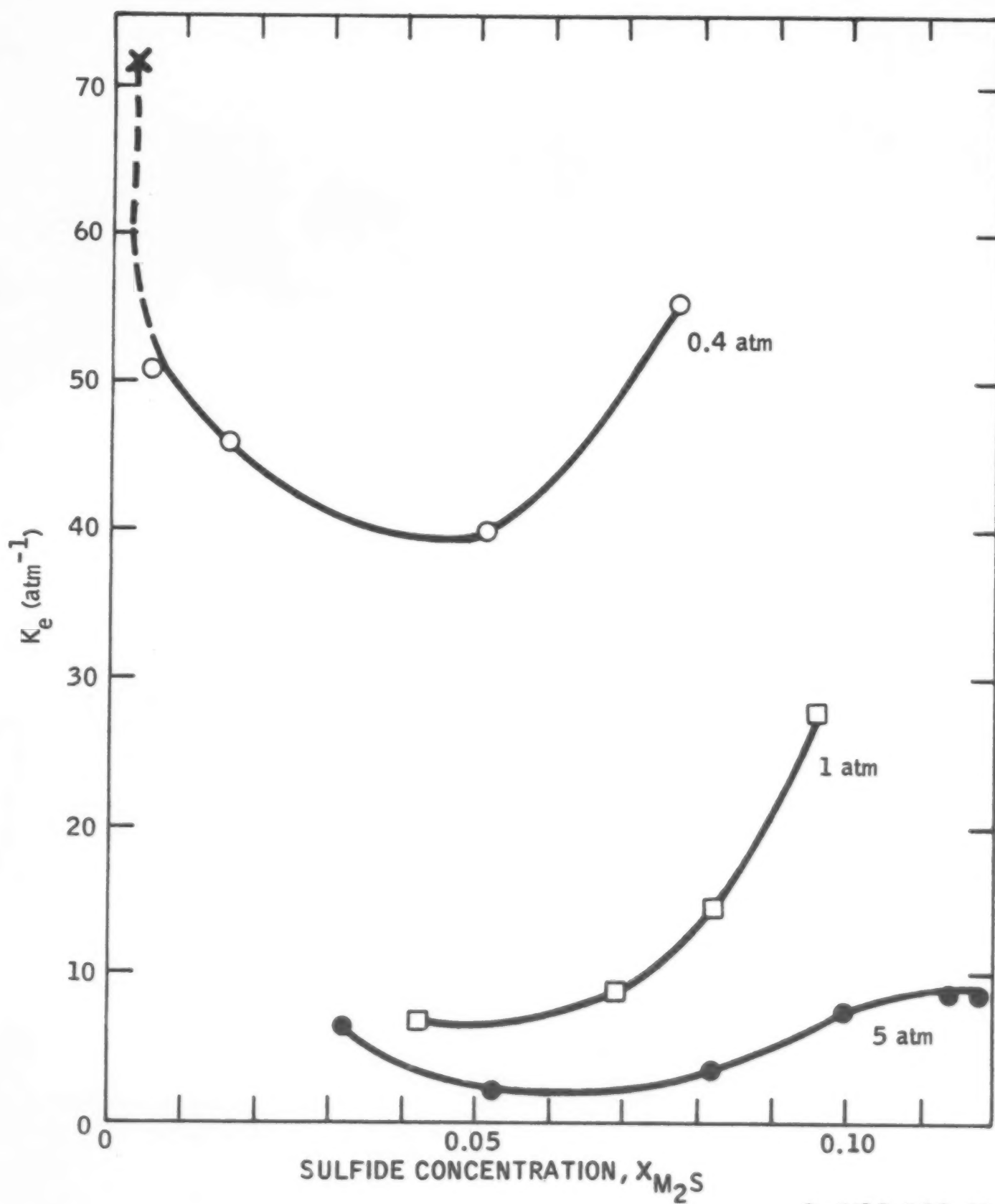


Figure 30. Regeneration Equilibrium Constant as Function of Melt Sulfide Concentration



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Figure 51. Dependence of Equilibrium Constant on Melt Sulfide Concentration and Reactant Pressure

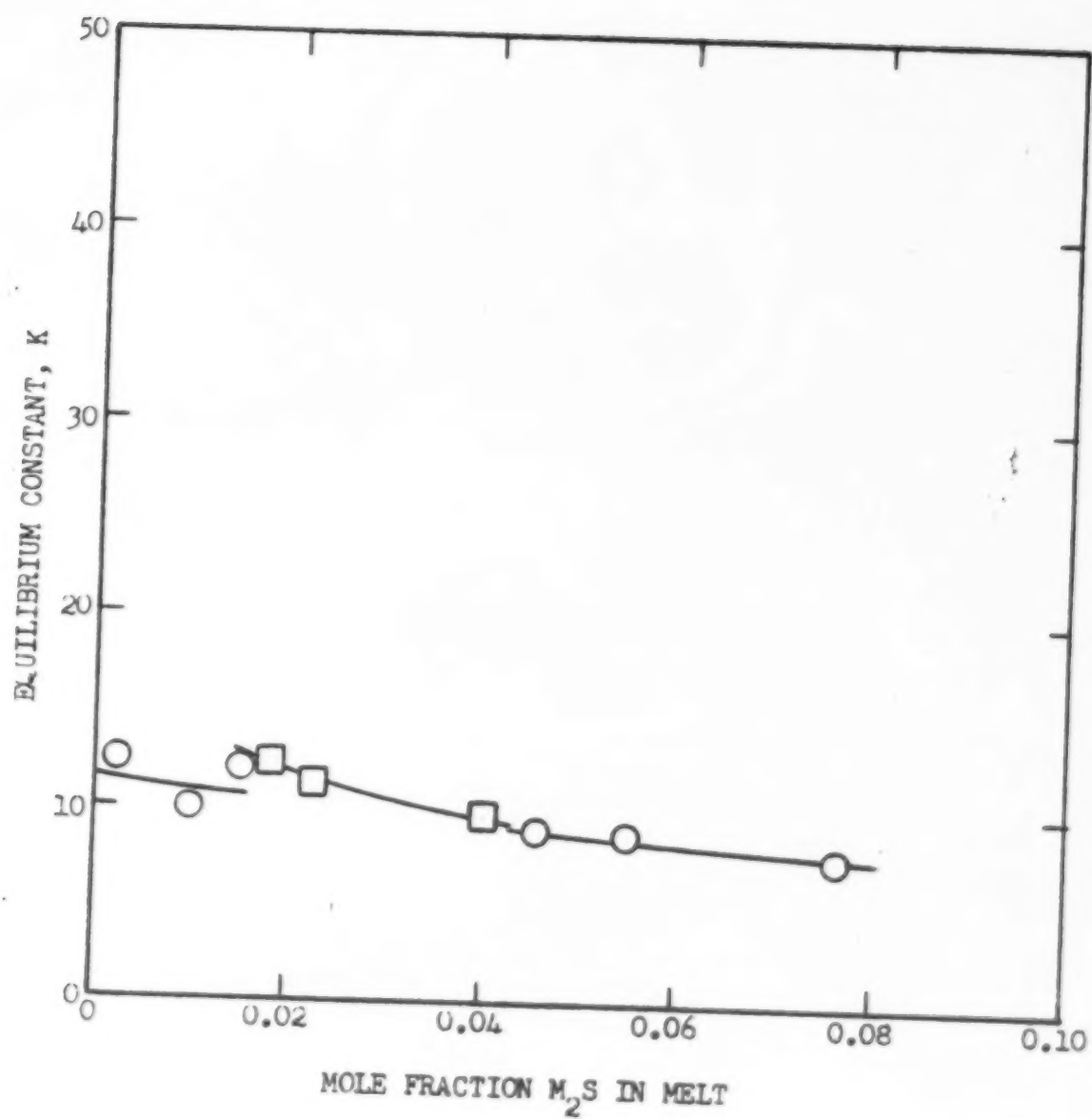
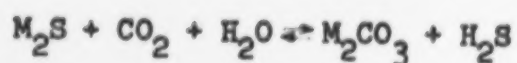


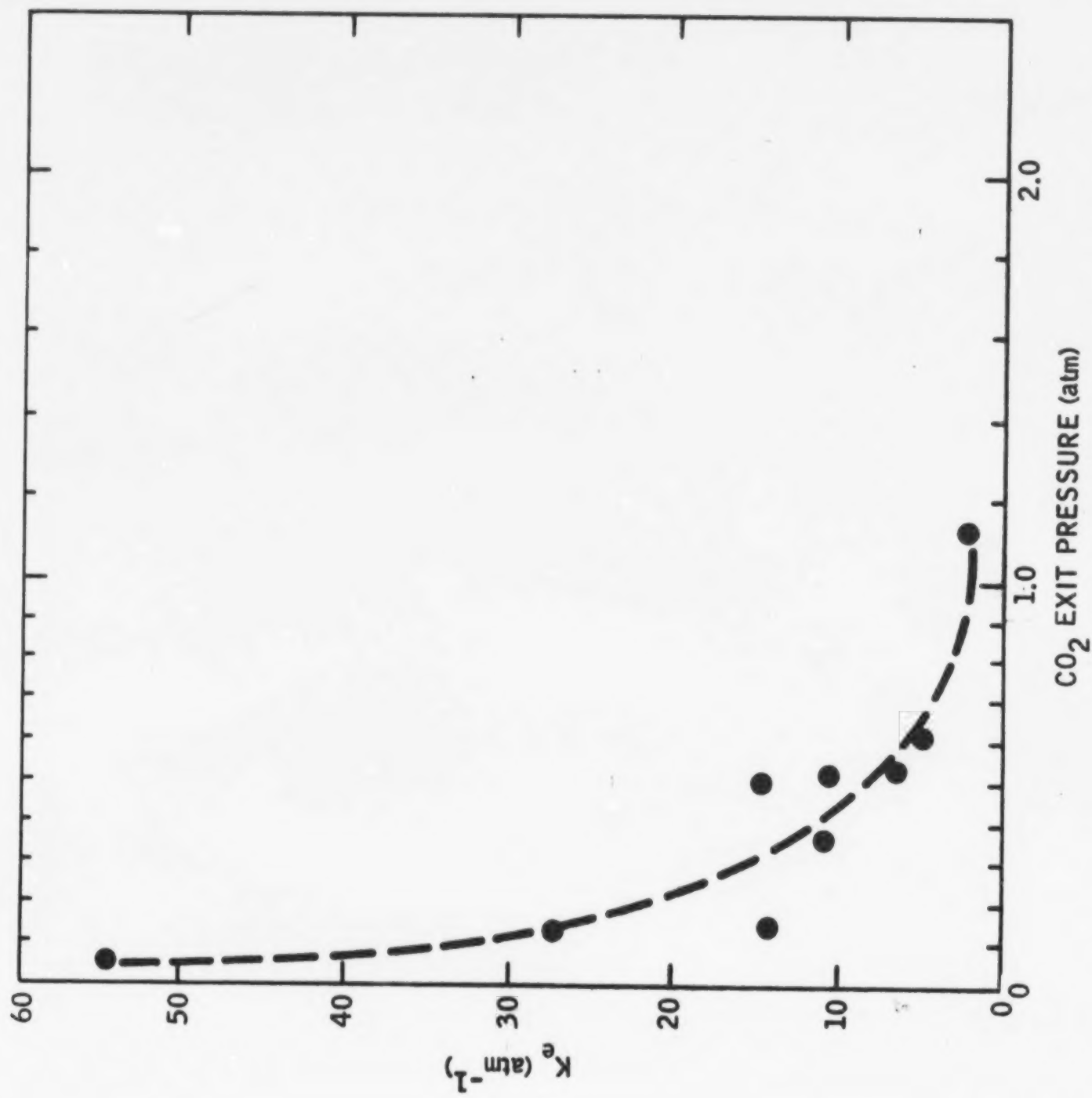
Figure 52. Equilibrium Constants for Regenerations at Low Inlet Gas Flow Rates

The plots shown in Figures 50 and 51 show that the equilibrium constant calculated according to expression 14 varies with pressure and probably with melt sulfide concentration. In Figure 51, the values for the effective equilibrium constant at 0.4 atmosphere pressure were 5 to 7 times those calculated at 1 and 5 atmospheres pressure. The value appears to be dependent on the sulfide concentration. The values for K start to increase rapidly at sulfide concentrations above 0.07 mole fraction for the three tests at different pressures. However, the partial pressures of the reactants, carbon dioxide and water, are also changing (decreasing) as the sulfide concentration increases. The large variations in the values for K_e could be caused by a side reaction involving one or both of these reactants. The regeneration reaction,



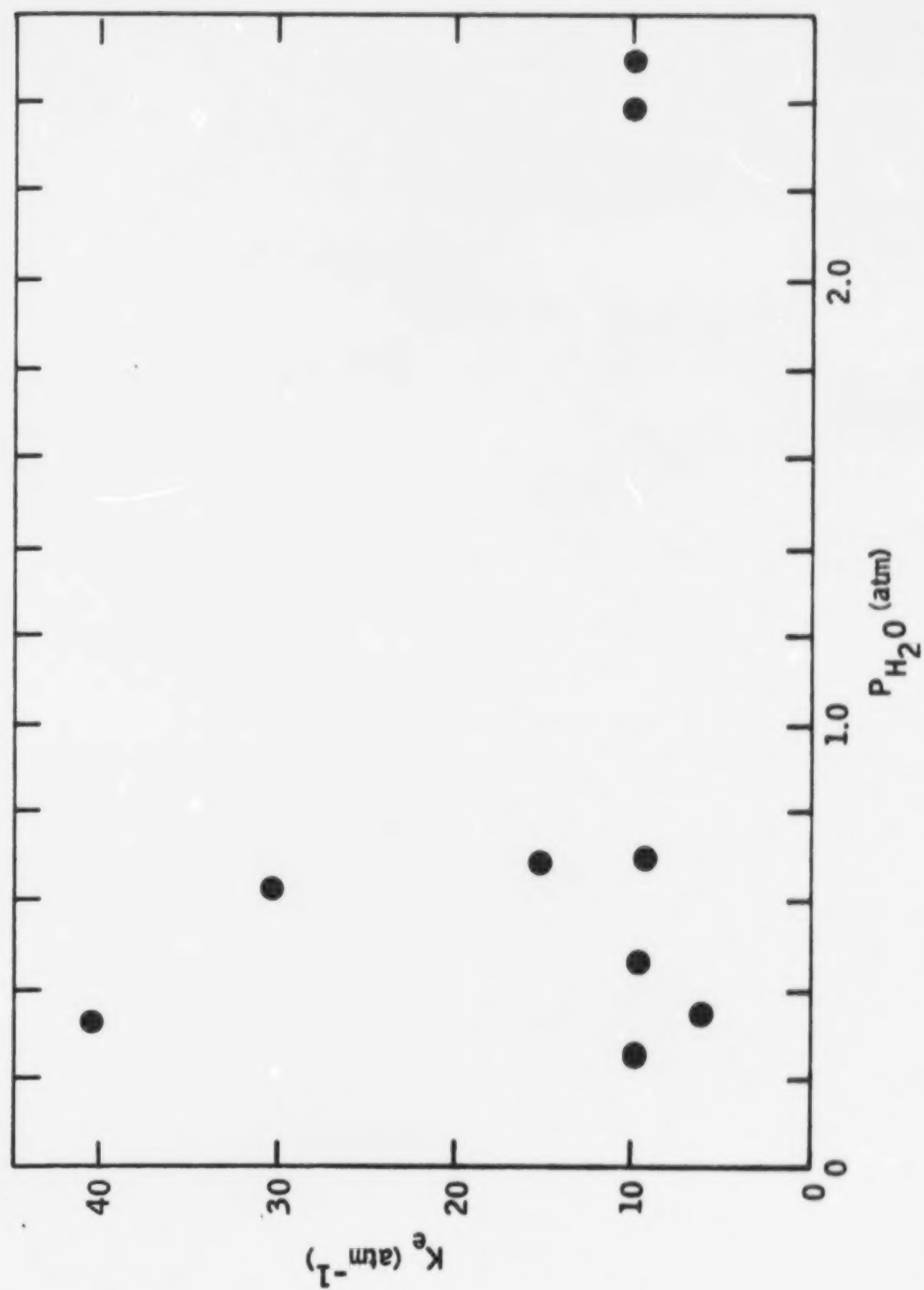
is the only important overall reaction which gives substantial gaseous products and which goes to completion; but during the regeneration, there are other reactions which could effectively reduce the activity of the sulfide.

As mentioned above, the effluent pressures of the reactant gases carbon dioxide, water vapor and hydrogen sulfide are continually changing. To see if there was some correlation between the calculated value for K and the effluent partial pressure of one of the reactants, a plot of K at various effluent pressures of carbon dioxide was prepared as shown in Figure 53. The plot shows that K is probably strongly dependent on the effluent or equilibrium carbon dioxide pressure. A similar plot of K vs P_{H_2O} (effluent) (Figure 54) shows no pronounced correlation, although a few more data points at high (1-2 atm) water vapor pressure are needed to make certain. Thus it



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Figure 53. Dependence of Equilibrium Constant on Carbon Dioxide Pressure



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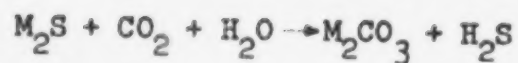
Figure 5A. Dependence of Equilibrium Constant on Water Vapor Pressure

appears that the value for the equilibrium constant varies with the carbon dioxide equilibrium pressure and not the total pressure of the reactants. As mentioned earlier, a tentative explanation for the carbon dioxide pressure effect is based on the interaction of carbon dioxide and sulfide in molten carbonates to give a series of mono-, di- and tri-thiocarbonates. An expression can be derived (see following part) based on equilibrium reactions involving thiocarbonates which shows that the value of K should vary inversely with the pressure of carbon dioxide. The observed variation of K_e with carbon dioxide pressure represents semi-quantitative evidence that carbon dioxide reacts with sulfide dissolved in carbonate melts. Qualitatively it has been observed that sulfide-bearing melts adsorb more carbon dioxide than pure carbonate melts and also, sulfide-bearing melts release adsorbed carbon dioxide much more slowly than pure eutectic carbonate melts. This effect was studied in more detail in order to obtain more quantitative data on the extent of the interaction in experiment 5 (see part E, section III).

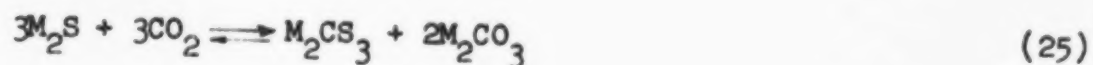
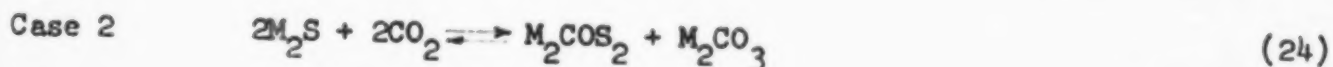
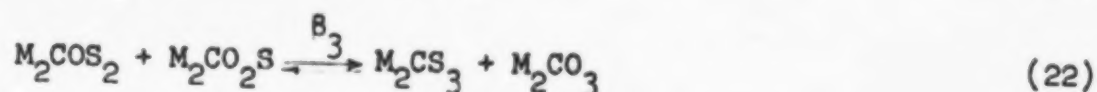
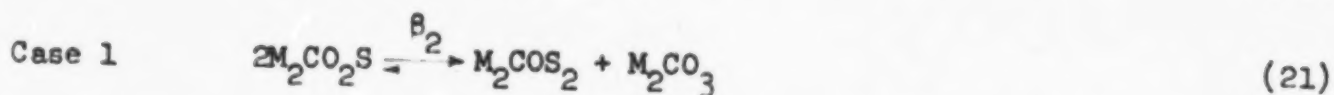
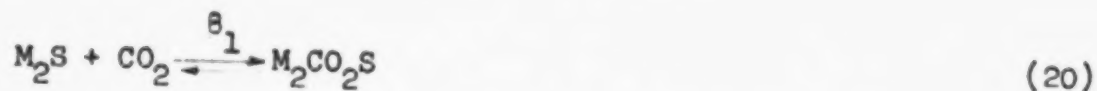
D. DERIVATION OF AN EXPRESSION FOR THE EFFECTIVE EQUILIBRIUM CONSTANT AS A FUNCTION OF SULFIDE CONCENTRATION AND CARBON DIOXIDE PRESSURE

An expression showing that the effective equilibrium constant is inversely dependent upon the carbon dioxide pressure is derived below. This derivation is based on three assumptions:

1. Equilibrium conditions are maintained during the regeneration process.
2. The only reaction which removes significant amount of gaseous products from the melt when the process is carried to completion is the usual regeneration reaction:



3. Carbon dioxide reacts with sulfide in the melt to form a series of mono-, di- and tri-thiocarbonates. The thiocarbonates might be formed in a series of sequential reactions (case 1) or each thiocarbonate (mono-, di- and tri-) may be formed directly (case 2) according to the postulated reactions:



Whichever sequence or series of reactions (Case 1 or Case 2) takes place, the overall effect on the free sulfide concentration (M_2S) can be shown to have the same dependence on carbon dioxide pressure. Thus, if $(M_2S)_T$ represents the total sulfide in the melt and (M_2S) represents the concentration of the unreacted sulfide, i.e., the activity of sulfide in the melt, then the total sulfide, $(M_2S)_T$, can be expressed as the total of all the possible sulfur containing species:

$$(M_2S)_T = (M_2S) + (M_2CO_2S) + 2(M_2COS_2) + 3(M_2CS_3) \quad (26)$$

Substituting the equilibrium expression in terms of (M_2S) , (M_2CO_3) and P_{CO_2} for the 2nd, 3rd and 4th terms on the right of the above expression gives:†

$$(M_2S)_T = (M_2S) + \frac{A(M_2S)(P_{CO_2})}{(M_2CO_3)} + \frac{B(M_2S)^2(P_{CO_2})^2}{(M_2CO_3)^2} + \frac{C(M_2S)^3(P_{CO_2})^3}{(M_2CO_3)^2} \quad (27)$$

Thus, the activity of sulfide in the melt (using the mole fraction of the free M_2S as its activity) can be expressed in the following form:

$$(M_2S) = (M_2S)_T / [1 + \frac{A(P_{CO_2})}{(M_2CO_3)} + \frac{B(M_2S)(P_{CO_2})^2}{(M_2CO_3)^2} + \frac{C(M_2S)^2(P_{CO_2})^3}{(M_2CO_3)^2}] \quad (28)$$

The equilibrium constant which has been calculated from regeneration reaction data was calculated according to the following expression:

$$K = \frac{(M_2CO_3)P_{H_2S}}{(M_2S)_T P_{CO_2} P_{H_2O}} \quad (29)$$

where $(M_2CO_3) = X_{M_2CO_3}$ and $(M_2S)_T = X_{M_2S}$ as determined by analysis. If one uses the actual sulfide concentration (M_2S) instead of $(M_2S)_T$ (for concentrations of $M_2S \leq 20$ mole %, the solvent concentration can be considered constant for a first approximation), then the correct formula for the equilibrium constant would be:

$$K_{corr.} = \frac{(M_2CO_3)(P_{H_2S})}{(M_2S)_T P_{CO_2} P_{H_2O}} [1 + \frac{A(P_{CO_2})}{(M_2CO_3)} + \frac{B(M_2S)(P_{CO_2})^2}{(M_2CO_3)^2} + \frac{C(M_2S)^2(P_{CO_2})^3}{(M_2CO_3)^2}] \quad (30)$$

† $A = \beta_1$, $B = 2\beta_2$, $C = 3\beta_3$

or

$$K_{\text{corr.}} = K[1 + A(P_{\text{CO}_2}) + \dots] \quad (31)$$

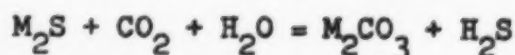
Thus, the value of K calculated according to equation (29) should vary inversely with P_{CO_2} and also show some dependence on M_2S concentration. That is, from (31)

$$K = \frac{\text{Constant}}{\left[1 + A(P_{\text{CO}_2}) + \frac{B(M_2S)(P_{\text{CO}_2})^2}{(M_2CO_3)} + \frac{C(M_2S)^2(P_{\text{CO}_2})^3}{(M_2CO_3)^2} \right]} \quad (32)$$

The experimentally observed pressure dependence of K on P_{CO_2} indicates that the 3rd (and possibly the 4th) term in the denominator of the right hand term of equation (32) are important. The values for the constants A, B and C cannot be evaluated from the present data. A better approach to evaluating these constants would appear to be the separate study of the carbon dioxide and sulfide reaction in molten carbonates.

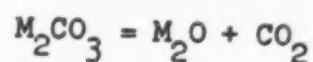
E. STOICHIOMETRY OF THE REGENERATION PROCESS

The amount of water consumed during the regeneration process corresponded closely to that expected from the regeneration reaction



The amount of carbon dioxide consumed appeared to be somewhat more than required on the basis of the above reaction. The material balance data were obtained on regeneration tests on reduced melts. The carbon dioxide required might be expected to vary depending upon the reducing conditions. For example, higher reduction temperatures with hydrogen might be expected to result in a

greater extent of carbonate dissociation:



Thus, more carbonate dioxide would be required over that needed for regeneration of the sulfide in order to replace that lost during the reduction process.

Table 24 shows the material balance data obtained on several regeneration tests. A more detailed study of the stoichiometry will be justified when the reduction conditions are specified in more detail.

TABLE 24

Material Balances for Several Regeneration Tests on Reduced Melts

Regeneration Test No.	Reactant	Total in Feed Gases (g)	Total Recovered (g)	Amount Needed (g) ^a	Reactant Unaccounted for (Used-Needed)
1	CO ₂	82	56.0	17.6	9
	H ₂ O	70.4	63.3	7.1	0
8	CO ₂	48	22.9	9.1	16
	H ₂ O	72.7	69.8	3.7	-0.8
9	CO ₂	42	15.7	14.1	12
	H ₂ O	50.2	42.3	5.8	2.1
10	CO ₂	31	21.3	11.3	-1
	H ₂ O	55.4	47.5	4.6	3.3
2	CO ₂	59	23.1	15.2	14
	H ₂ O	77.5	70.2	5.3	2

^aBased on reaction, $M_2S + CO_2 + H_2O = H_2S + M_2CO_3$ and on the amount of H₂S recovered.

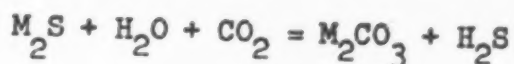
F. TREATMENT OF SULFIDE-BEARING MELTS WITH CARBON DIOXIDE AND WATER VAPOR SEPARATELY

In most of the regeneration experiments, the melts were reacted with mixtures of carbon dioxide and water. In several cases, melts were treated with dry carbon dioxide initially. It was found that the carbon dioxide treatment promoted reactions (e.g., carbonyl sulfide generation) which were not significant when water was present. There was a possibility that the treatment of sulfide melts separately and successively with carbon dioxide and then water could also provide data useful for interpreting the reactions which are important in the regeneration process. In addition, the treatments could provide data which would give the amounts of carbon dioxide or water stored in the melt.

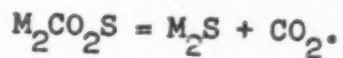
In one regeneration test, a reduced sulfide melt was treated with the regeneration gases (carbon dioxide and water vapor) in separate and successive steps (Test No. 16, Table 3). Figures 20a, 20b and 20c show plots of the effluent gas compositions versus time. The melt was first treated with a dry carbon dioxide-helium mixture until the effluent gas composition remained essentially constant at about 35 vol% CO_2 , 1.8 vol% COS , and 0.6 vol% H_2S . This occurred after about two hours of carbon dioxide treatment. The relatively long time required to reach a constant effluent gas composition resulted from the absorption of carbon dioxide during the first stages of the treatment. The major part of this absorption was due to the reaction of carbon dioxide with sulfide (Experiment 5, Section III-F). Carbon dioxide would have reacted with any oxide, hydroxide, bicarbonate or bisulfide anions if these were present in the melt after the melt had been reduced. The small amount of hydrogen sulfide present in the effluent during the dry carbon dioxide treatment indicates that only small amounts of chemically-bound water

could have been present in the reduced melt. Thus, the amount of hydroxide or bisulfide in the melt would be of the order of 1% or less. It appears that hydroxide could be present since hydroxyl ions are stable to some degree in lithium carbonate.⁽⁷⁾ Oxide, if present in the melt, should absorb stoichiometric amounts of carbon dioxide. Since the reduced melt did not appear to absorb an appreciably larger quantity of carbon dioxide than did a synthetic sulfide melt (made from Na_2S , K_2CO_3 , and Li_2CO_3), the amount of oxide produced during the hydrogen reduction process must have been small also.

The effect of water vapor treatment on a reduced melt that had previously been treated with dry carbon dioxide resulted in the evolution of appreciable amounts of hydrogen sulfide. Since carbon dioxide was present in the off gas, most of this hydrogen sulfide could be produced as a result of the regeneration reaction



with the carbon dioxide coming from the reaction



After the first water vapor treatment, the melt was purged for ten minutes with helium and then treated with dry carbon dioxide and helium again. The amount of hydrogen sulfide evolved during this carbon dioxide treatment was about 4 to 5 times that evolved during the initial treatment after the reduction at 600°C. This indicated that the melt retains more water at the lower temperature (500 vs. 600°C) and that the water may be stored chemically as bicarbonate or bisulfide. However, the amount stored was still relatively small, in the range of 1-2 mole percent bicarbonate or bisulfide in a melt containing 20 mole percent sulfide.

G. EFFECT OF METAL CATIONS OTHER THAN ALKALI METAL CATIONS ON THE REGENERATION REACTION

The study of the effects of impurities upon the regeneration process involved introducing foreign metal cations in the sulfide-bearing melt. These impurities consist of metal ions (other than alkali metals) which may be added intentionally for some beneficial effect or unintentionally as corrosion products or fly ash products. In all cases, the foreign metals were introduced into a sulfate melt which was reduced with hydrogen. The sulfide-bearing melts were then regenerated in the usual manner. The effect of a particular metal impurity can be evaluated by observing what effect the metal had upon the effluent gas composition during the regeneration test and upon the total sulfur recovery after completion of the test. The impurities could be grouped into four different classes depending upon the nature of their effects upon the regeneration process.

TABLE 25

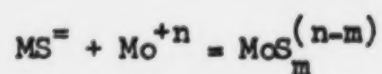
Classifications of Metal Impurities as to their Effect on the Regeneration Reaction

Class of Impurity	Effects on Regeneration Reaction	Metals	Regeneration Test No.
1	No noticeable effect	Ca*	20
2	Reduced H ₂ S content of effluent, high sulfur recovery as H ₂ S	Mo V	6 7
3	Reduced H ₂ S content of effluent, low sulfur recovery as H ₂ S (< 5%)	Sn Ge	4 5
4	Reduced H ₂ S content of effluent, moderate sulfur recovery as H ₂ S (40-70%) Impurity forms insoluble compound containing sulfur. Presence of impurity in certain forms, causes salt to foam.	Fe	8, 9, 10, 11, 12... (see Table 3)

* Cations of the other alkaline earth metals and alkali metals are expected to be in this classification.

Calcium showed no noticeable effect on the regeneration process. The thermodynamics for the regeneration of calcium sulfide are favorable and it is expected that other alkaline earth sulfides could also be regenerated without difficulty. Thus, a small amount of calcium from fly ash should not interfere with the regeneration step.

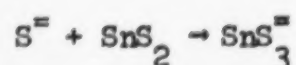
The principle effect of the metal ions of molybdenum and vanadium was to increase the time required for regeneration from about 180 to 300 minutes when compared to a regeneration test of sulfide melts containing no added metal impurities. This effect was probably a result of the lowering of the sulfide activity as a result of equilibrium reactions of the type



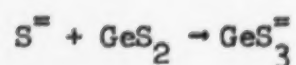
where n is the oxidation state of molybdenum in the melt. The value of n under the conditions existing in a regeneration process is not known. If most of the molybdenum were in the +4 oxidation state, the sulfide-molybdenum species which could be present in equilibrium concentrations would be Mo^{+4} , MoS^{+2} , MoS_2 , MoS_3^{-2} , etc. The behavior of the melt containing vanadium appeared to be similar. The fact that high sulfur recovery values were obtained (92 and 86% for melts containing molybdenum and vanadium, respectively) is evidence that the sulfide activity was reduced in these melts by reversible equilibrium reaction(s).

In the case of tin- and germanium-containing melts (class 3 impurity), the effect was similar to that observed with molybdenum and vanadium, except that the activity of sulfide was reduced to a much greater degree. Thus, only 4.2 and 5.7% of the sulfur was recovered from melts containing tin and germanium even though the regeneration process was continued for a five-

hour period. This suggested that the reduction of sulfide activity through association reactions, e.g.,



and



was much greater than in the case of melts containing molybdenum and vanadium. The oxidation states of tin and germanium in the melts were not known. X-ray diffraction patterns of a salt deposit formed above the melt line during the regeneration of the tin-containing melt indicated that both SnS and SnS_2 were present.

Iron is listed as a Class 4 impurity. The effects of iron on the regeneration process were substantially different from the effects of the other metal impurities. Iron is of particular importance especially because of (1) its value as a catalyst for the reduction process, and (2) the possible build-up of iron in the melt from corrosion and fly ash. Thus, the effect of iron on the regeneration process was examined in considerably more detail and is discussed in the following section.

H. THE REGENERATION OF MELTS CONTAINING IRON

The effects observed in the regeneration of reduced sulfide-bearing melts containing iron were (1) foaming of the salt during regeneration, (2) low sulfur recovery values (50-70% recovery) in one-cycle tests, and (3) the formation of insoluble materials containing iron and sulfur in the form of sulfides.

The first evidence (visual) that iron caused foaming was observed in cycle test nos. 1 and 2 (Table 8). In these tests, extensive foaming occurred during the regeneration steps. These melts had previously been made by reducing, with hydrogen, melts which had absorbed appreciable quantities of sulfur dioxide. These intended cycle tests were carried out with the melts contained in stainless steel vessels (347 S.S.) and they could not be completed because of excessive foaming during the regeneration step. In cycle test no. 1, when the exit lines became plugged during the regeneration step, a salt sampling port was opened and a copious amount of brown salt foam flowed from the reactor and solidified. The volume of the foam was approximately 3-4 times the original liquid volume of the salt in the reactor. Although iron had not been added to the salt in this test, substantial amounts of iron (and other corrosion products) were present in the melt after the reduction step as a result of corrosion of the stainless steel crucible during the reduction at elevated temperatures. It was not certain that iron and other possible impurities caused the foaming in the above cycle tests. However, the succeeding experiments with graphite crucibles and bubblers with controlled amounts of iron present, established the fact that iron does cause foaming during regeneration.

In a number of regeneration tests (test nos. 8, 9 and 10, Table 3), the volume of salt remaining in the bottom of the reactor crucible was considerably less than it was at the beginning of the regeneration process. Since no salt samples were taken during the reaction, this decrease in salt volume resulted entirely from a deposition of salt on the wall of the crucible and on the bubbler above the melt line. After most of the regeneration tests, the reactors were opened and inspected. In those cases where there was iron

in the melt prior to the start of the regeneration test, a substantial salt deposit was usually (but not always) found on the walls of the crucible. This deposit contained substantial amounts of iron (8-9 wt%) and sulfide (14-26 wt%) (Table 20). Since it was known that foaming occurs under certain conditions, the deposition of the salt deposit was attributed to foaming. Thus, the change in melt volume was indicative of the extent of foaming which had occurred during a regeneration test. Also, since iron and sulfide were concentrated in the deposit, the level of these components in the completely regenerated melt was also an indication of the extent of foaming. It is possible that the conditions during reduction and/or regeneration could affect the tendency of an iron-containing melt to foam and some qualitative evidence of this is discussed below.

The change in melt volumes for regeneration tests 8, 9 and 10 can be estimated from the test data given in Table 26.

TABLE 26

Loss of Salt due to Foaming During Regeneration
of Reduced Melts Containing 2.4 wt% Iron

Regeneration Test No. (from Table 3)	Reduction Temp., °C	Regeneration Temp., °C	Melt Volume Decrease, %
8	600	500	35
9	600	500	18
10	600	500	44
11	650	600	14
12	700	500	10
13	650	500	10
15	600	425	11

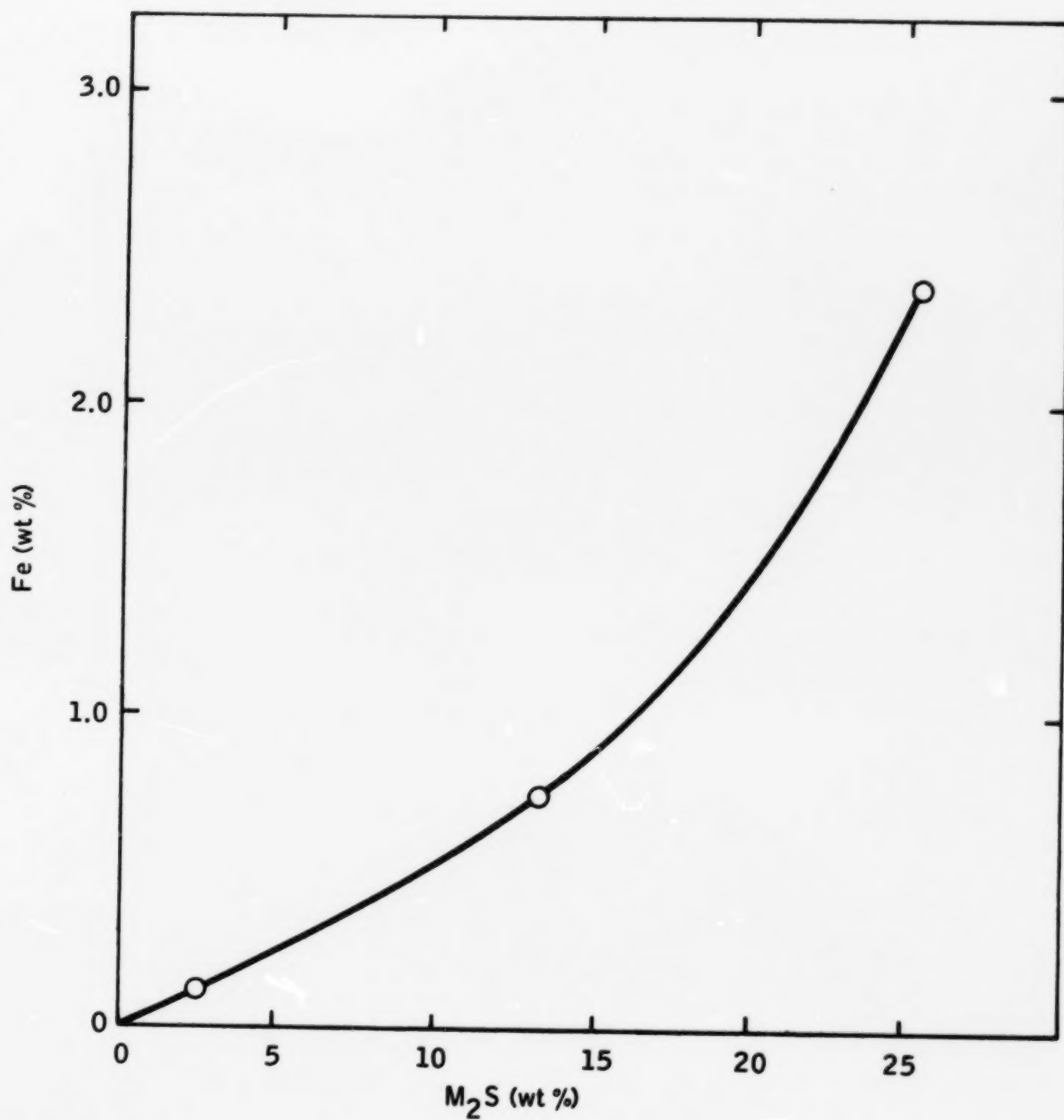
The melt volume decreased by 35, 18 and 44 percent. Thus the extent of foaming appeared to be substantial (volume change, 20-40%) when a melt containing iron had been reduced at 600°C and regenerated at 500°C. Using these conditions as a reference point, the comparison (qualitative) in Table 26 shows that the extent of foaming decreased as the reduction temperature was increased. Also, it appeared that the amount of foaming decreased with a decrease in the regeneration temperature. Other variables which appear to have affected the foaming characteristics of the reduced melt are reduction pressure and regeneration pressure. In test no. 24 (Table 3), less foaming was observed when the reduction pressure was 5 atmospheres; in test no. 26, less foaming was observed with higher regeneration pressure (5 atm). In addition, the use of carbon monoxide (without and with iron, tests 3 and 19) as the reducing agent instead of hydrogen resulted in melts which showed no evidence (no melt volume change) of foaming when they were regenerated at 500°C.

The fluid characteristics of the deposits which formed during the regeneration step can be described from the results of cycle tests 4 and 5 (Tables 10 and 11). From the results of these tests, it could be concluded that the deposits remained on the walls above the melt during the regeneration because they became solid or semi-solid at 500°C. The deposits could not be liquified by heating at 600°C in a hydrogen atmosphere (observed in cycle tests). The high temperature and reducing atmosphere could have resulted in a change in oxidation state of iron from Fe^{+3} to Fe^{+2} , the latter presumably forming a lower melting sulfide-carbonate mixture. Other oxidation-reduction reactions may be involved. This behavior indicates that the oxidation-reduction potential of the melt is important in regulating the

solubility of some components and that this effect may be important in the foaming behavior. The properties of the melt also appear to be important in the precipitation of iron during the regeneration process.

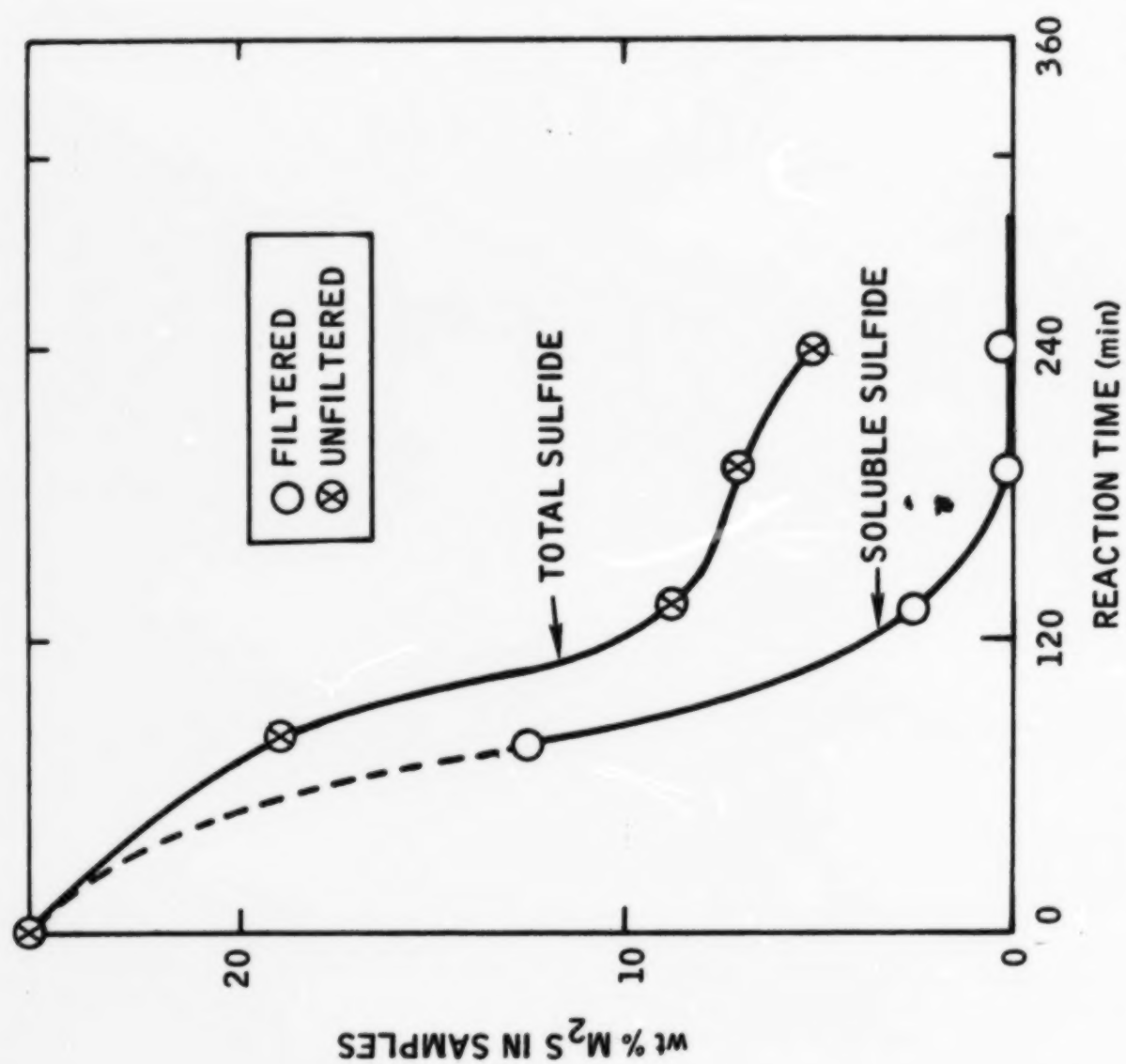
The solubility of iron in a melt during the regeneration process was investigated in regeneration test no. 17. As mentioned above, this melt did not foam during the regeneration process even though it contained iron and was reduced with hydrogen at 5 atmospheres pressure. The data in Table 5 show that the solubility (concentration of iron in filtered samples) of iron decreases rapidly as the sulfide concentration of the melt decreases from 25 to 0 mole percent. Figure 55 shows the solubility of iron plotted against sulfide concentration based on data obtained from regeneration test 17. The results also showed that some sulfide was being removed in the form of an insoluble material, since the filtered samples contained less sulfide than the unfiltered samples. Figure 56 shows a plot of total sulfide and soluble sulfide plotted against regeneration time.

The mole ratio of sulfur to iron in the precipitate during the initial period (first filtration) was 3.1 but decreased to 2, 2.2 and 1.7 for the remainder of the test. This suggested that two different iron sulfide compounds were precipitated. The ratio of 2:1 for the sulfur-iron ratio is in agreement with x-ray diffraction data (Table 20) which suggested the presence of $MFeS_2$ in froth deposits. The ratio of 3:1 may indicate the precipitation of a thiocarbonate of iron ($FeCS_3$) during the initial stages of the regeneration process. Additional data should be obtained to verify this one data point. Some additional evidence for the precipitation of an iron thiocarbonate was observed in regeneration test 23 in which both the iron and



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Figure 55. Iron Solubility as a Function of Melt Sulfide Content



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Figure 56. Decrease in Sulfide Solubility During Regeneration of Iron-Containing Melts

sulfide content of the melt decreased when the sulfide-bearing melt was treated with dry carbon dioxide.

The tendency of sulfide melts containing iron to foam during regeneration appears to be caused by the iron in the melt. The mechanism by which the foam is stabilized might be related to the fact that insoluble materials containing iron and sulfide are foamed during the regeneration process. These compounds may be surface-active, i.e., they may be positively adsorbed at the surface or interface. This would result in the formation of foams which are thermodynamically stable. The foam might also be stabilized if the particles of precipitate hold entrapped gas, or release gases at their surfaces. More experimental data are required to understand the mechanism of foam stabilization in the regeneration process. The experimental data do suggest possible methods of reducing the tendency to foam, but until the reducing conditions and agents are specified in more detail, further experimental study of this effect would probably not be justified.

I. CYCLE TESTS

The results of cycle tests 3, 4 and 5 (Table 8) demonstrated several important points regarding the molten carbonate sulfur dioxide removal process. Cycle test 3 results (Table 9) showed that the molten carbonate did not degrade in its capacity to remove sulfur dioxide after reduction-regeneration steps. Cycle test 5 results (Table 11) showed that (1) the sulfur added to the melt after the first cycle could be completely recovered in succeeding regeneration steps, and (2) that the iron catalyst, recovered after each regeneration step, could be used in successive reduction steps without a detectable loss in effectiveness as a catalyst.

J. LIMITATIONS ON THE RATE OF REGENERATION

After the analysis of data from several regeneration tests had been completed (section D, Discussion), it was apparent that equilibrium conditions were maintained during the bubble-through tests even at fairly high input gas flow rates. Thus, it was suggested that increasing the input rate of the regeneration gases should cause the sulfide concentration to decrease faster and at a predictable rate, based on the value for the effective equilibrium constant determined from the tests at low input gas feed rates.

Assuming an effective equilibrium constant of 10 atm^{-1} , the melt sulfide concentrations as a function of regeneration time at several different ratios of regeneration gas feed rate to melt volume were calculated. These curves (sulfide concentration versus time) were plotted as the solid curves in Figure 57. The equilibrium expression predicted that complete regeneration could be achieved in 40, 80 or 140 minutes at feed rate to melt volume ratios of 1.28, 0.64 and 0.32 moles/minute per liter, respectively. However, it was not known if equilibrium could be maintained at such high gas flow rates in the bubbler contactors used. Three tests (Regeneration Tests 29, 30 and 31) were carried out to investigate this, using the standard regeneration test procedure. The regeneration gas was formed by bubbling dry carbon dioxide through a water saturator, with the saturator temperature adjusted to yield a mixture of 50% water vapor. The total feed rate was regulated by regulating the carbon dioxide flow rate.

The results of the three tests are shown plotted as the dashed curves in Figure 57. The sulfide contents of the three melts decreased about as predicted, with the data points all falling on or below the theoretical curves. In addition, the test data (regeneration test no. 29) at a feed gas

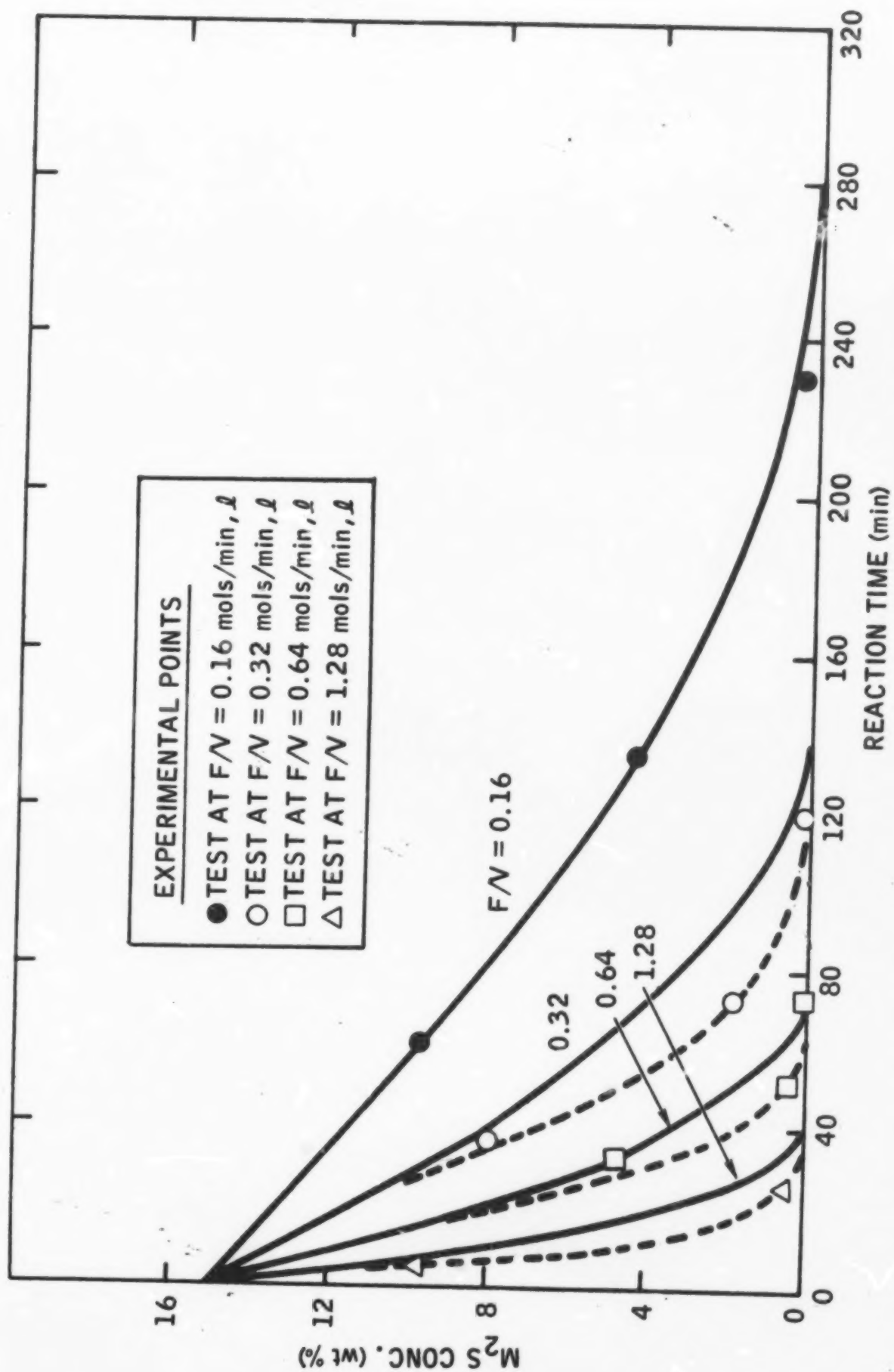


Figure 57. Regeneration at High Flow Rates

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flow rate to melt volume ratio value of 0.16 moles per minute per liter, fell on the curve corresponding to that ratio. This indicates that equilibrium was attained, even at the highest feed rate to melt volume ratio. The difference between the theoretical and experimental results is probably due in part to inaccuracies and fluctuations in the water saturator temperature, and in part to the change in the amount of conversion with the equilibrium carbon dioxide pressure.

The most rapid regeneration was done with a feed rate to melt volume ratio of 1.28 mole/min. per liter. This actually corresponded to carbon dioxide and water vapor flow rates of 1600 ml/min. each and a melt volume of 100 ml. Since equilibrium was evidently maintained in a simple bubbler even at this high gas throughput rate, the regeneration reaction(s) must be very rapid. It is quite probable that regeneration times significantly less than the 40 min. can be achieved at higher gas throughput rates.

VII. SUMMARY AND CONCLUSIONS

The regeneration tests have involved the study of regeneration reaction in a relatively broad range of experimental conditions. The experimental variations which were studied during the course of the investigation are classified as follows:

1. Variation in sulfide-bearing melts

a. Methods of preparation

b. Impurities

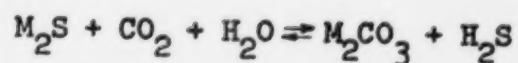
(1) Metal cations other than alkali metal cations present in melt

(2) Anions other than carbonate and sulfide present in melt

2. Variations in feed gases
 - a. Variation in H_2O to CO_2 feed ratios
 - b. Effect of diluents in feed gas
 - c. Variation in feed gas input rates
3. Variation in temperature
4. Variation in pressure
5. Variation in reactor design.

The important effects of the variations on the regeneration process will be discussed below.

The basic reaction



has been found to be the important overall reaction. The equilibrium for this reaction is attained rapidly under all test conditions. The conditions including temperature, pressure and impurity levels wherein the equilibrium is favorable for a rapid and complete conversion to pure carbonate and hydrogen sulfide can be specified.

The initial investigations on the regeneration reaction started with attempts to carry out the reaction in rotating reactors filled with iron screws to improve contact surface. Only limited amounts of sulfur (4-7%) could be recovered as hydrogen sulfide in these tests and the difficulty was found to be in the retention of much of the sulfur by the corrosion products from the screws and the steel bomb.

Tests were begun in bubble-through reactors with the intention of improving the contact if necessary. The first tests involved sulfide melts made by reducing sulfate melts with hydrogen in a short time period, high

carbon dioxide (3 l/min and 0.9 l/min) flow rates were used. Both of these tests had to be terminated because of extensive foaming of the melt. It was later proved that this foaming was caused by the presence of appreciable amounts of corrosion products (notably iron) which had accumulated in the melt during the reduction step.

The subsequent regeneration tests were carried out using graphite crucibles and graphite bubblers with sulfide-bearing melts containing little or known amounts of impurities. At this time a large number of such melts were being provided as a result of the reduction studies. These melts were being prepared through the reduction of sulfate-bearing melts with hydrogen under various test conditions and with a variety of materials present in known amounts as potential catalysts for the reduction step. These melts were regenerated with carbon dioxide and water under the same experimental conditions from test to test with only minor variations. This was done so that effects of variation in the reduction tests on the regeneration reaction could be identified or recognized.

As a result of the regeneration studies on sulfide-bearing melts made by reduction with hydrogen in the presence of a variety of possible catalysts, the effect of these various impurities on the regeneration process was established. These effects are discussed above in the section on impurity effects.

Also as a result of the regeneration of various reduced melts, several pertinent questions arose which could not be resolved from results of a single regeneration test. These problems were caused by the presence of iron in the melt during the regeneration step. They were important because iron was effective as a catalyst in the reduction of sulfate by hydrogen. The significant questions were (1) could the sulfur be completely recovered as hydrogen

sulfide from sulfide melts containing iron and (2) could the iron be recovered conveniently from a regenerated melt and reused as a catalyst? These questions were answered affirmatively by carrying out additional cycle tests (cycle tests 3, 4, 5, Table 8). In addition, several special experiments (regeneration test 17, Table 5; tests 2, 5, Table 17) were carried out in which a melt containing iron was filtered during stages of the regeneration tests; these tests established that iron sulfide compounds were relatively insoluble in regenerated carbonate melts but that they were more soluble in carbonate melts containing excess sulfide.

The regeneration tests on the reduced melts and the cycle tests resolved most of the questions involving complete sulfur recovery, catalyst recovery, stoichiometry of the regeneration process, and the effects of impurities and of several reduction step variables on the regeneration reaction. Two other important areas which needed to be studied were the time required to complete the regeneration of a sulfide melt and how to optimize the effluent gas composition. These two are related in a sense that a high hydrogen sulfide content of the effluent gas insures a fast regeneration under a given gas to liquid volume ratio. Hence it was necessary to optimize conditions for the most favorable effluent gas composition (maximum hydrogen sulfide content) and also to determine whether there were any kinetic limitations to attaining equilibrium conditions.

The regeneration tests which were carried out to establish conditions for optimizing the effluent gas composition and to study rate limitations involved sulfide melts made both by the reduction process and by sodium sulfide addition synthetic sulfide melts. The first tests (cycle test 6) involved regeneration tests wherein the pressure of the system was varied. Since the

regeneration reaction involves two gaseous reactants and one gaseous product, it was expected that the higher pressures would increase the hydrogen sulfide content of the effluent gas. From this study of the pressure effect on the regeneration reaction, it was found that the opposite was true; that is, the relative amount of hydrogen sulfide to carbon dioxide and water in the effluent was greater at lower system pressures than at higher pressures. This was subsequently attributed to the interaction of carbon dioxide with sulfide-bearing melts. The explanation for this effect is discussed above. This pressure effect was clearly demonstrated through a detailed analysis of several regeneration tests carried out at different pressures. This analysis involved calculations of the apparent equilibrium constant at various stages of each regeneration. This analysis showed that the calculated equilibrium constant varied during the course of the regeneration of a melt in a batch type process and varied considerably from one test to the next depending upon the total pressure of the system. This analysis was discussed in detail in section VI.

Other methods of optimizing the effluent gas composition involved a study of the temperature effect on the equilibrium and the effect of the inlet carbon dioxide to water vapor ratio.

From published work⁽²⁾ mentioned earlier on the reaction of solid sodium sulfide and potassium sulfide with carbon dioxide and water and from calculations based on thermodynamic data it was known that the regeneration reaction was more favorable at the lower temperatures; but the magnitude of this effect in the molten carbonates could not be determined except by experiment. Thus, regeneration tests were carried out at temperatures above and below and at 500°C to establish the effect of temperature. The effect of the carbon dioxide

to water vapor was studied theoretically prior to the discovery of the carbon dioxide pressure effect and this theoretical effect was discussed in section VI.

The attempts to determine whether there were any kinetic limitations to obtaining equilibrium in the regeneration reaction were the main objectives of the last four regeneration tests listed in Table 6. These tests were carried out under similar conditions except that in each successive test the feed gas flow rate to melt volume was doubled over that used in the previous tests. Under these conditions, the change in the melt sulfide content could be compared with a theoretical prediction based on attainment of equilibrium during the contacting. It was found that the melt sulfide content did decrease as fast or faster than predicted in each case and therefore indicated that there were no kinetic limitations under the experimental conditions used.

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